IDENTIFICATION OF INDUSTRIAL SOURCES OF AIRBORNE HEAVY METAL POLLUTION IN URBAN AREAS.

STEPHEN ANDREW SIMMONS

A Thesis Submitted in Partial Fulfilment of

the Degree of

DOCTOR OF PHILOSOPHY

Department of Civil Engineering

The University of Aston in Birmingham

OCTOBER 1984

THE UNIVERSITY OF ASTON IN BIRMINGHAM

IDENTIFICATION OF INDUSTRIAL SOURCES OF AIRBORNE HEAVY METAL POLLUTION IN URBAN AREAS

STEPHEN ANDREW SIMMONS

A Thesis Submitted in Partial Fulfilment of the Degree of Doctor of Philosophy

1984

SUMMARY

The research examines the deposition of airborne particles which contain heavy metals and investigates the methods that can be used to identify their sources. The research focuses on lead and cadmium because these two metals are of growing public and scientific concern on environmental health grounds.

The research consists of three distinct parts. The first is the development and evaluation of a new deposition measurement instrument - the deposit cannister - designed specifically for large-scale surveys in urban areas. The deposit cannister is specifically designed to be cheap, robust, and versatile and therefore to permit comprehensive high-density urban surveys. The siting policy reduces contamination from locally resuspended surface-dust.

The second part of the research has involved detailed surveys of heavy metal deposition in Walsall, West Midlands, using the new high-density measurement method. The main survey, conducted over a six-week period in November - December 1982, provided 30-day samples of deposition at 250 different sites. The results have been used to examine the magnitude and spatial variability of deposition rates in the case-study area, and to evaluate the performance of the measurement method.

The third part of the research has been to conduct a 'source-identification' exercise. The methods used have been Receptor Models - Factor Analysis and Cluster Analysis - and a predictive source-based deposition model. The results indicate that there are six main source processes contributing to deposition of metals in the Walsall area: coal combustion, vehicle emissions, ironfounding, copper refining and two general industrial/urban processes.

A source-based deposition model has been calibrated using factorscores for one source factor as the dependent variable, rather than metal deposition rates, thus avoiding problems traditionally encountered in calibrating models in complex multi-source areas. Empirical evidence supports the hypothesised association of this Factor with emissions of metals from the irontoundry industry.

AIR POLLUTION, SOURCE IDENTIFICATION, DEPOSITION, LEAD, CADMIUM

ACKNOWLEDGEMENTS

For their contributions to this work I acknowledge the assis tance of my sponsors,the Science and Engineering Research Council and the Environmental Health Department of Walsall Metropolitan Borough;and my acedemic supervisors Dr Robert Pocock and Dr Tom Chidley.

CONTENTS

List of Tables

List of Figures

List of Plates

CHAPTER 1

A GENERAL REVIEW OF THE RESEARCH PROBLEM

1.1 Introduction to the research

1.1.1 Overview

This thesis addresses the problem of deposition of heavy metals in urban areas. Specifically it focusses on three important issues: firstly, the basic problem of measuring the rate of deposition of heavy metals in urban areas; secondly, the related question of assessing the degree of spatial variability in deposition rates in urban areas; and thirdly, the question of explaining this spatial variability by relating the observed spatial distribution of heavy metal deposition to the known distribution of sources of atmospheric emissions.

1.1.2 Summary of the research area

In recent years an awareness has developed that some heavy metals emitted by anthropogenic activity are accumulating in the environment to the point where human health may be at risk. Two metals in particular are the cause of public and scientific concern; they are lead and cadmium.

Lead is historically one of the most widely dispersed of environmental pollutants. There is increasing scientific debate about the human toxicologial significance of those body burdens of lead that are

insufficient to cause 'clinical' symptoms of poisoning, but are nevertheless present in a large number of individuals in the population. Specifically, concern is being expressed about the possible effects of low levels of lead on the intelligence and behaviour of young children (see section 1.2.3).

In contrast to lead, cadmium has only recently become widely dispersed to the environment as a result of man's activities. However, there is concern over the possible long term health implications of increased environmental exposure to cadmium (section 1.2.3). This concern has been aroused partly by individual incidents of cadmium poisoning (for example the cases of Itai-Itai disease in certain villages in Japan) and partly by the rapid increase in the quantities of cadmium used and discharged by industry since the 1940's.

The uncertainty over the potential health implications of increased exposure of the population to both lead and cadmium has prompted increased scientific research into the importance of various sources and pathways that may contribute to individual exposure. However, many of these sources and pathways are poorly understood. Deposition of airborne particulates is one important mechanism by which atmospheric emissions may contaminate soil, dust and food crops and so contribute to the pathways leading to human exposure. However, comparatively little is known about this mechanism particularly in respect of the ambient deposition of heavy metals in urban areas. This research has therefore been designed specifically to investigate the deposition of heavy metals in urban areas, and so contribute to an improved scientific understanding of the general problem of heavy metal pollution.

1.1.3 Synopsis of Chapter 1

This first chapter of the thesis aims to introduce the broad research area, and to describe the investigative framework within which the research project was carried out.

Section 1.2 reviews the fundamental research issue, namely the relationship between human health and the accumulation of heavy metals in the environment. Section 1.3 directs attention to the fact that the problem of heavy metal contamination and human exposure is likely to be most severe in industrial urban areas. In section 1.4 the specific objectives of this research project are outlined, and in section 1.5 the research methods are described. The broad conclusions of the research together with the thesis structure are summarised in section 1.6.

1.2 Health effects and environmental accumulation of lead and cadmium

1.2.1 Definition

There is some confusion in the literature concerning the definition and use of the terms 'heavy metal', 'trace metal' and 'toxic metal'. The descriptive term 'heavy metal' has been used in this research and in definition has been taken to apply to those metals having a specific gravity of greater than 5, as previously defined by Passow et al (1961). The lanthanides[1] and actinides[2] were not included as they are not generally considered as being 'heavy metals' (Nieboer and Richardson, 1980).

1.2.2 Toxicity of the heavy metals

In the literature on environmental research the term 'heavy metal' tends to be used where there are connotations of toxicity. However, most metals can be toxic if present in large enough quantities. This is true even of biologically essential elements such as: copper and zinc (Underwood, 1977). The relative toxicity of metals is in fact best understood in terms of the concept of a 'concentration window'. This term is used to describe the range of concentrations that are compatible with normal biological functioning. Outside

---

1 The lanthanides are those elements of the periodic table between barium and hafnium, otherwise called the rare earth elements.

2 The actinides are those elements of the periodic table following radium.

the 'window', concentrations below the minimum biological requirement may initiate deficiency symptoms, while concentrations in excess of the concentration window may produce toxic reactions. Metals can be classified as 'trace metals' when they perform a biologically useful purpose and the concentration window is at low concentration, for example, copper, chromium, nickel and zinc can be described as trace metals, as well as heavy metals (Underwood, 1977). Metals such as cadmium, lead and mercury which serve no known biologically useful purpose and are only tolerated in very low amounts are the 'toxic metals' (Tucker, 1972).

Toxicity of heavy metals may vary significantly according to a wide range of factors; for example the route of entry into the body (Fell, 1980); nutritional factors (Fox, 1974, and Baltrop and Khoo, 1975); and age and sex. For some of the more toxic heavy metals the chemical form of the metal intake is also important (organo-metal compounds generally being more toxic than elemental or inorganic compounds). These factors mean that 'dose-response' relationships are often uncertain; while one population group may tolerate a specific metal uptake, in another group this may prove toxic. This has meant that there have been great difficulties in deciding what constitutes a 'safe' level of environmental exposure. However, for three of the more toxic heavy metals - cadmium, mercury and lead - there has been widespread medical concern that in certain circumstances, human exposure may be approaching or exceeding the 'safe' levels (Royal Commission on Environmental Pollution, 1983). These three metals can therefore be identified as 'priority' metals from viewpoint of pollution control, and priorities for research on these metals in the environment are now well established (Department

of the Environment, 1976 for mercury, Department of the Environment, 1980 for cadmium and Department of the Environment and Welsh Office 1982 for lead).

In the following sections toxicological issues concerning lead and cadmium are discussed in detail. These two metals were selected as priority metals for the purposes of this research. Mercury has not been included because the practical difficulties involved in its detection make it difficult to carry out experimental/field work involving its measurement. This is a pragmatic decision and should not be taken as any indication of an underestimation of its relative toxicological significance.

1.2.3 Health effects of low levels of exposure to lead and cadium

Clinical symptoms of acute lead and cadmium poisoning are rare. They are generally observed only in cases of accidental poisoning or in cases of excessive occupational exposures (Browning, 1961). Chronic poisoning may occasionally be observed in cases of exceptional environmental exposures (for example the case of Itai-itai disease observed in certain Japanese villages resulting from high environmental exposure to cadmium). However, there is growing concern that the current lead and cadmium population exposure of certain 'at risk' population groups, although insufficient to cause acute or chronic poisoning, may nevertheless induce sub-clinical or asymptomatic health effects, or that critical doses may be reached in certain target organs as a result of long term exposure and accumulation.

Some of the evidence for this possible environmental health problem is now reviewed. Lead and cadmium are considered separately in turn.

There is intense scientific debate over the possible effects of low-levels of lead on the intelligence and behaviour of young children (these form the most at risk target group in the general population). Some studies have claimed that environmental exposure can produce measurable effects in children as determined by their performance in intelligence and behaviour tests. Conversely, other studies have failed to find any effects due to lead and attribute differences between different exposure groups to confounding factors (e.g. recent papers by Needleman et al, 1979; Millar et al, 1981; Thatcher et al, 1982; and Lansdowne et al, 1983).

The findings of these reports have been extensively reviewed (e.g. Department of Health and Social Security (1980) - the Lawther Report, Bryce-Smith and Stephens (1980) the Conservation Society reply, and the Royal Commission on Environmental Pollution (1983)).

The uncertainties surrounding the health effects of low-levels of exposure to lead have prompted investigations to determine what body burdens of lead are found in various target groups of the population. The results of these surveys have indicated that certain population groups may exceed 'safety levels' (for example the Department of the Environment (1982b) 25 mg/dl blood lead level): typically adults living in the vicinity of industrial lead sources and areas where the water supply is plumbo-solvent, and children living in inner cities (for example Department of the Environment 1981a, 1982 and 1983).

Instances of Itai-itai disease in Japan have been attributed to the intake and uptake of high levels of environmental cadmium (Nogawa, 1981). However, very little information exists on the health effects of long-term low level exposure for the general population.

Cadmium accumulates in the kidney (one of the specific target organs where damage occurs at concentrations of between 100-300 ppm wet weight (World Health Organisation, 1977)). Attempts have been made to extrapolate data from the Itai-itai studies to possible environmental concentrations and exposures which could result in kidney concentrations of 200 ppm; best estimate of 100-300 ppm (e.g. Friberg et al, 1984 and Council and European Communities, 1978). Lauwreys et al (1981) have found evidence of cadmium related kidney damage in elderly multiparae (females with many offspring) in an area of elevated environmental levels. However, in the Somerset village of Shipham, where the soil has been highly contaminated by cadmium wastes from a local mining operations (Davies and Ginnever, 1979), no evidence of health damage has been found. Other possible hazards concern possible cardio-vascular effects, possible carcinogenicity, possible foetal effects and effects at a sub-cellular level, however little information exists on the likelihood of these occurring at general levels of exposure.

1.2.4 Accumulation of lead and cadmium in the environment

Like many of the heavy metals, lead and cadmium are persistent and once discharged to the environment may accumulate in 'sinks' such as soil and dust. Long-term accumulation resulting in elevated levels has been observed in the vicinity of roads (Davies and Holmes,

1972), industrial sources (Little and Martin, 1972 and Davies and Roberts 1975) and in urban gardens and dust (Davies et al 1979 and Harrison, 1979). Both soil and dust may be important contributors to human exposure either through food or direct adventitious ingestion, so contamination of these specific media may present a hazard to the population. However, the passive accumulation and long residence times (Tyler, 1978) means that there is not only widespread human exposure today, but future generations too will be exposed to these metals which are already in the environment and are being supplemented by present day sources and emissions. For this reason it is important to understand the mechanisms by which metals move through the environment from their sources to the routes of human intake. These mechanisms and pathways are considered in the following section.

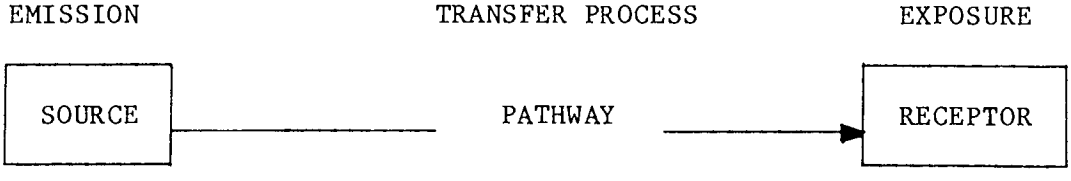
1.3 The environmental pollution process and human exposure in urban areas

1.3.1 Introduction

Lead and cadmium are multi-media pollutants, present in the atmosphere, hydrophere, biosphere and lithosphere. The main features of the global cycle of lead and cadmium are illustrated in figures 1.1 and 1.2, respectively. From these cycles it is evident that on a world-wide basis anthropogenic activity releases over 24 times as much lead and 9 times as much cadmium to the atmosphere than is emitted by natural processes. This section discusses how these anthropogenic emissions may affect the environment and human exposure in circumstances where there is the greatest concentration of both sources and population; urban areas.

1.3.2 The heavy metal pollution process

In order to understand how heavy metals emitted by anthropogenic sources may afect human exposure it is necessary to identify the key routes through which metals may be transfered. At a global scale a simple environmental model can be defined (as in figures 1.1 and 1.2). In a similar fashion the environmental pollution process linking sources and exposure can be represented as a simple model:



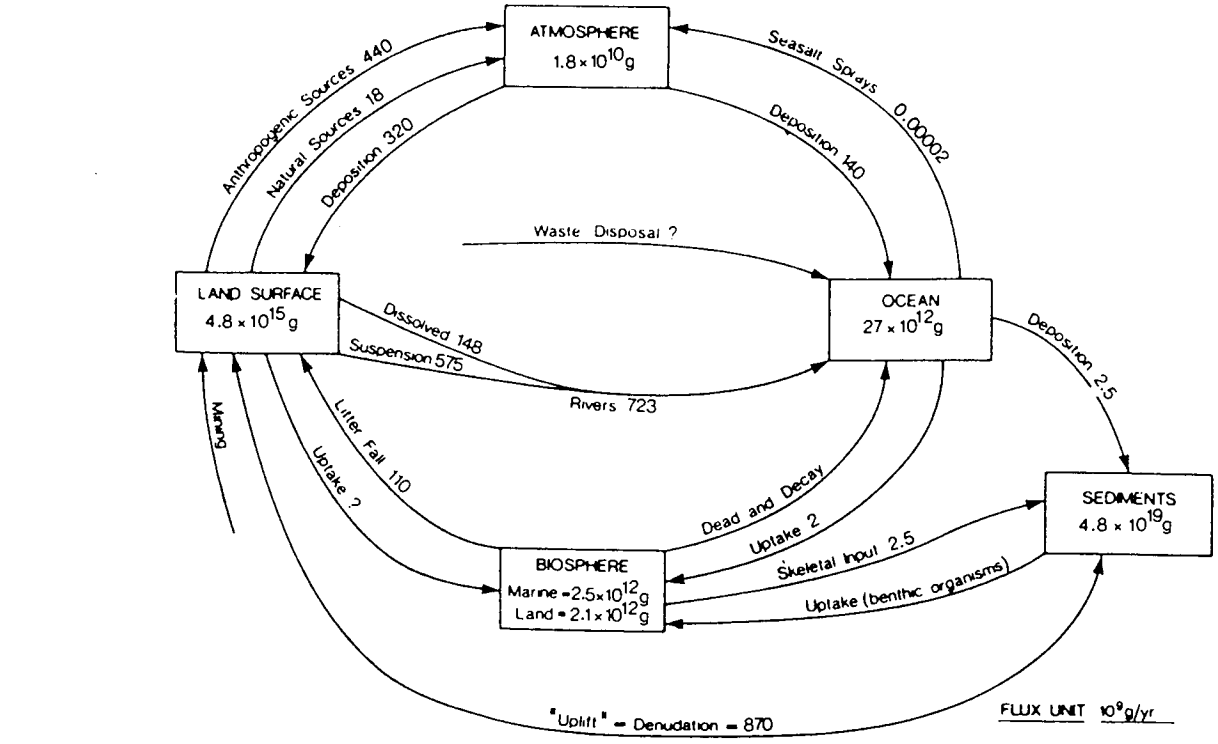


FIGURE 1.1 GLOBAL LEAD CYCLE (From data given by Nriagu, 1978)

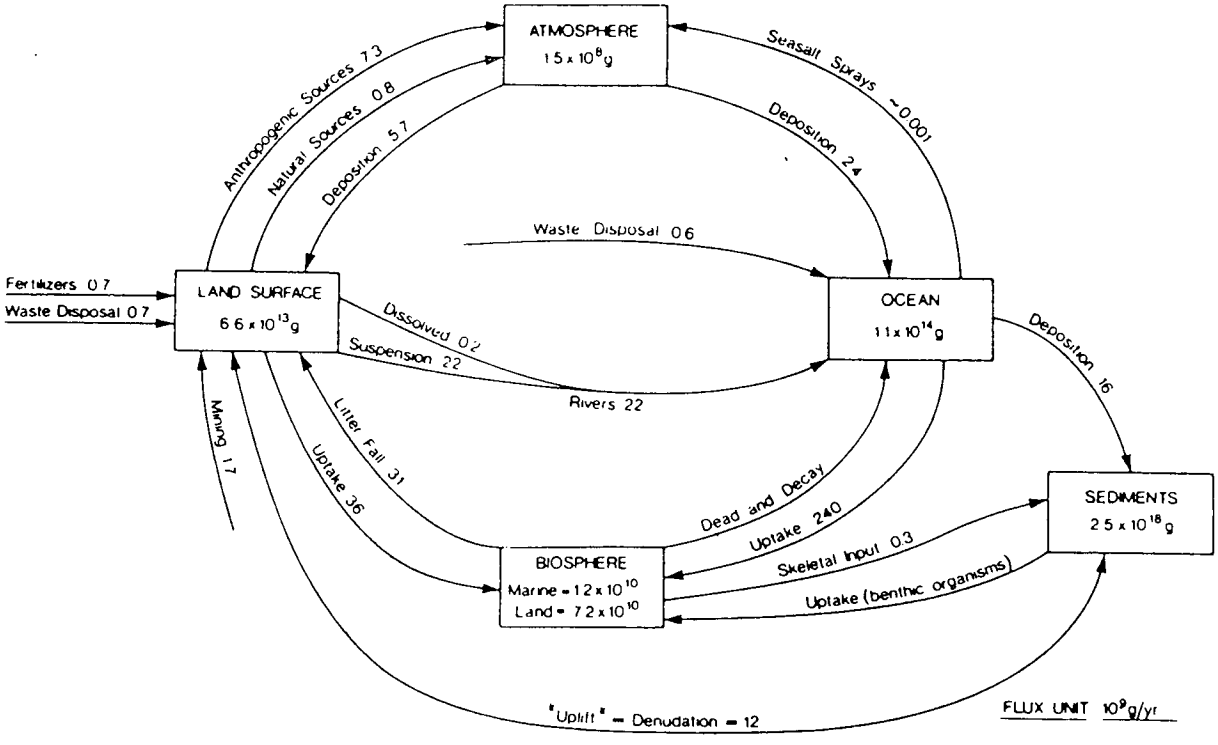


FIGURE 1.2 GLOBAL CADMIUM CYCLE (From Nriagu, 1980).

In some cases of excessive human exposure this pollution process is easy to follow because the transfer process is transparent. For example in the case of Itai-itai disease in the region of Japan referred to in paragraph 1.2.3 above, the source of the cadmium was easily identified as being a local zinc mine which was contaminating river water and rice crops. In most situations however, the pollution process is poorly understood, because the multiplicity of contributing sources and the diversity and complexity of the transfer pathways makes it difficult to establish scientifically the links between human exposure, environmental pathways and original sources. The effectiveness of environmental management and protection policy is consequently limited by the uncertainties that make it difficult to evaluate the costs and benefits of control policy options.

1.3.3 Human exposure pathways

Human exposure to lead and cadmium in the urban environment may be taken as an example where the pollution process is poorly understood. While there are a great many factors influencing individual human exposure, contemporary research has indicated that for both lead and cadmium, contaminated food is an important route of metal intake (Ministry of Agriculture, Fisheries and Food, 1981; Department of the Environment, 1980) , other environmental exposure routes may be locally important:

(1) ingestion of lead and cadmium in soil and dust (Duggan, 1980 and Tennant, 1984). This pathway may be particularly important for young children who

have been estimated to ingest about 0.1 g/day from sucking fingers and contaminated objects (Duggan and Williams, 1977),

(2) lead in water supplies (Department of the Environment and Welsh Office, 1982),

(3) inhalation of lead and cadmium in airborne particulate matter and cigarette smoke (Harrison and Laxen, 1981, Lewis, 1972),

(4) ingestion of lead in paint (Cooney and Blake, 1982).

The processes whereby soil may become contaminated by heavy metals are broadly of four kinds:

(a) exploitation of mineral resources;
(b) application of metal-bearing sewage sludge;
(c) site contamination by former industrial use;
(d) deposition of airborne heavy metal particulates.

The first three represent localised problems, while deposition is a general and widespread process by which not only soil, but dust and the leaves of crops may become contaminated by emissions to the atmosphere. This pathway represents a '<u>critical point</u>' in the pollution transfer process represented in figure 1.3. Many details of this pathway are poorly understood. Both the Royal Commission to the Environmental Pollution (1983) and the Commission of the European Communities (1981) have highlighted this as a priority

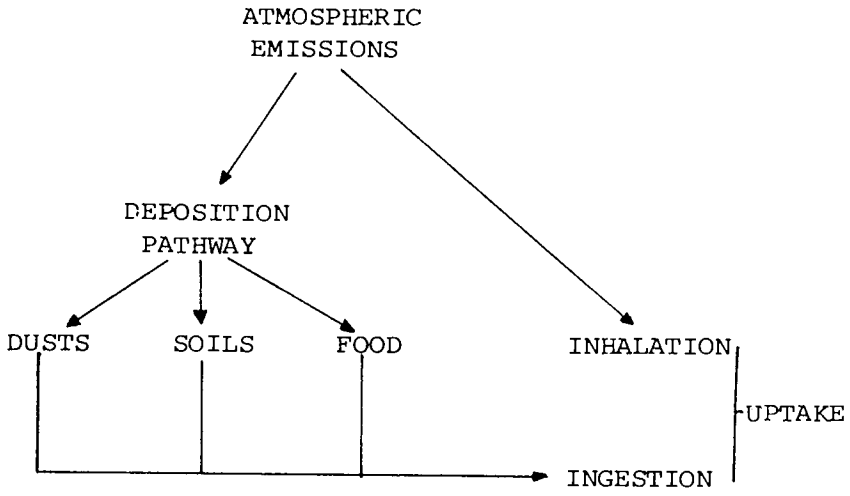


FIGURE 1.3 The Environmental Pollution Process
(⟶ Transfer pathway.)

area for further research. In the Federal Republic of Germany (F.D.R.), the potential significance of lead and cadmium deposition has been recognised and maximum standards for lead and cadmium deposition rates have been proposed (Weber, 1981). Chapter 5 contains details of these standards. In the United Kingdom the principle of controlling metal input to soils is recognised (Agricultural Development and Advisory Service (1971) and the Department of the Environment (1981b) have prescribed maximum rates of addition in sewage sludges applied to land), but there is as yet no formal guidance on acceptable or undesirable levels of general airborne deposition of metals.

1.3.4 Lead and cadmium in deposition: the urban problem

In general, the largest concentration of anthropogenic sources of lead and cadmium occurs in urbanised areas. While isolated examples of lead and cadmium pollution can be found in non-urban areas (for example fallout in the vicinity of isolated metal smelters) the numbers of people who are exposed are small, i.e. the problem is localised. In urban areas however, there is a large population potentially exposed and the level of exposure is potentially highest. It is therefore in urban areas that any environmental health problem is likely to be most acute. In Chapter 2 the general levels of lead and cadmium deposition are shown to be elevated in urban areas when compared to levels in rural and remote regions. However, current data are based on surveys with relatively few sampling stations and low sampling densities. Very little is known about the spatial variability of metals in deposition in urban areas and so it is difficult to judge the representativeness of the results of these surveys in characterising an entire urban area.

1.3.5 Research aim

This research therefore tackles the problem of measuring, representing and explaining the spatial pattern of heavy metal deposition (specifically for lead and cadmium) in urban areas. In this way the study as a whole focus es on the circumstances where the transfer of metals from source to receptor through the critical point of deposition are most acute and poorly understood.

1.4 Research Framework

1.4.1 Introduction

The purpose of this section is to summarise the three research objectives that derive from the broad research aim stated in the previous paragraph, within a general research framework as represented in figure 1.4

1.4.2 First Objective (Ob.1): Measuring/Quantifying heavy metal deposition rates

There are two ways of obtaining measurements of deposition. Firstly the deposition onto a surrogate natural surface can be collected and used as an indicator of the net rate of metal accumulation in a particular type of medium (e.g. the moss bag technique). However this is critically dependent on the nature of the surface used and is therefore only a measure of net metal input. The second approach is that of quantifying the gross vertical flux of metal deposition by using collection containers into which downward moving particles may fall, such as the standard British Deposit Gauge (B.S.D.G as detailed in B.S. 1747) and the International Standards Organisation Deposit Gauges (ISOG as detailed in ISO DIS4222.2).

These two instruments form the basis of most contemporary studies of airborne particulate deposition. However they are bulky, they require special support frames and stands, they require siting in secure locations to avoid vandalism and wind damage and are expensive to purchase and maintain. These constraints have in the past severely restricted the number and density of sampling sites that have been

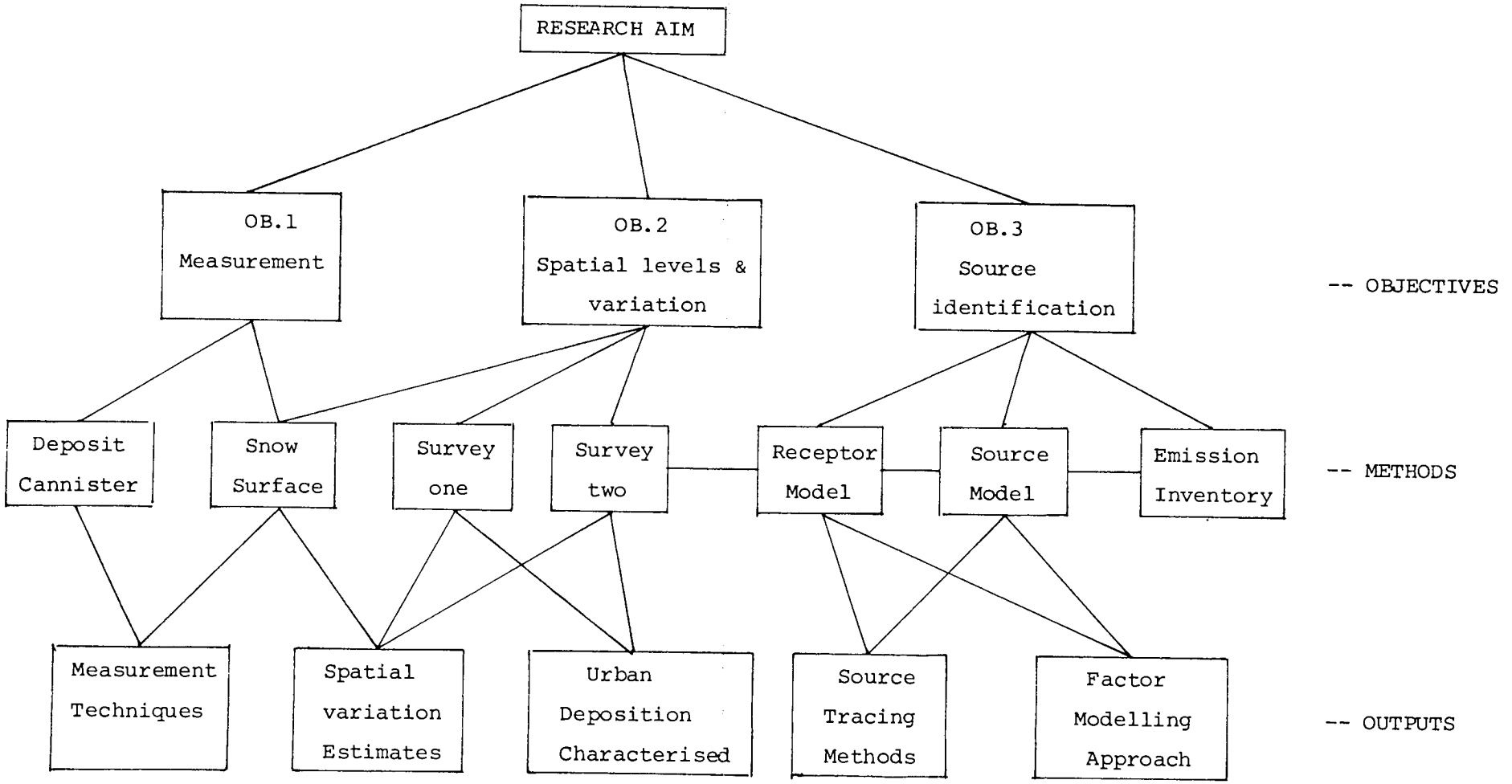


FIGURE 1.4 The Research Framework.

used in surveys of urban areas. There are also questions over the choice of an appropriate siting height of these instruments typically a height of 1.5 m above the ground is used, but this is a height which may expose the gauge to contamination by locally resupended surface dust. The first objective of this research was specified in response to these practical difficulties and has been:-

> Ob.1 - to explore the deposition measurement process and to develop and evaluate a deposition measurement method that is suitable for large scale surveys in urban areas.

1.4.3 Second Objective (Ob.2): studying spatial variability in the deposition rates of heavy metals.

Previous research on the deposition of heavy metals has been restricted by the measurement difficulties discussed above. There has been a tendency for instruments to be sited in such a way as to examine specific problems (e.g. deposition in the vicinty of industrial works) and general ambient deposition in urban areas has consequently been poorly researched. For example Duggan and Burton (1983) rely on only 8 measurments sites to characterise deposition in the entire Greater London area. While such surveys are interesting in that they relate to deposition around specific sources, there is no indication as to how representative these sites are of deposition in the wider vicinity. If deposition is highly spatially variable (as is the case for soil metal levels is urban areas (Pocock, 1982)), then a high density of sampling points would be required to adequately represent the characteristics of deposition across part or all of an urban area. The second objective of this research has therefore been:

Ob.2 - to explore the levels and spatial variability of heavy metals in deposition in urban areas

1.4.4 Third Objective (Ob.3): source identification

Ob.1 and Ob.2 were formulated in response to the scientific need for better data on the deposition of heavy metals in urban areas. However the problem of metal contamination in the urban environment provokes both a scientific and policy related need to explain the occurrence of metals in the deposition pathway by relating the observed levels to their component sources. In previous surveys sources have been inferred (for example Little and Martin 1972) or identified on the basis of physical and meteorological factors (e.g. Clayton, 1981). However, these surveys have all involved localised problems. There have been no attempts to identify and quantify the component sources of general urban deposition. This is largely due to the large number of potential sources that are present in urban areas. This multiplicity of individual sources and source types complicates the task of apportioning an observed deposition level to specific sources. But it is just such circumstances that would benefit most, scientifically and in the context of environmental management, if the relationship between sources and deposition were to be more fully understood. The third objective of the research has therefore been:

Ob.3 - to investigate the relative significance of different sources of heavy metals in deposited particulate matter.

This section has outlined the theoretical framework for the research

in terms of three objectives. In the following section the research methods used in the research are described in terms of the ways in which they respond to the research objectives. Figure 1.4 is useful in this context as it illustrates which methods serve which objectives and indicates the interactions that exist between the methods.

1.5 Research Methods

1.5.1 Introduction

This section briefly describes the research methods that were used to satisfy the research objectives, within the obvious time and resource constraints of a postgraduate research project. Detailed reviews of the measurement process and techniques of source identification are given in Chapters 2 and 3 respectively, while the experimental design is considered in Chapter 4.

1.5.2 Case-study investigation of Walsall

For the specific purpose of this investigative research programme it was decided to apply the methods in the form of a case-study of an urban area. Walsall Metropolitan Borough was selected for this case-study because it satisfied the two main technical criteria in having been demonstrated to have elevated environmental heavy metal levels (in airborne particulate matter (e.g. Pattenden and Branson 1982), soil (Pocock, 1982), dust. (Walsall Environmental Health Department, 1983) and deposition (Pattenden and Branson 1982)) and there is a wide variety of land-uses in the area. Walsall is also located within reasonable distance of the University of Aston and their Council Officers were willing to co-operate in the study through the mechanism of a CASE Studentship.

1.5.3 The Measurement of Deposition

To satisfy Ob.1 (1.4.2) and also to enable a large number of

deposition measurements to be made for the purposes of Ob.2 and Ob.3, a new sampling instrument was designed. This instrument consists of a simple plastic cannister (the Deposit Cannister), 6 cm in diameter and 12 cm deep, which is equivalent to a reduced scale (½ size) I.S.O.G. These cannisters were mounted on specially designed clip brackets, and sited by attaching to convenient supports (mainly telegraph poles) at a height of 6 m above ground level. This height, substantially above the 1.5m of the conventional B.S.D.G and I.S.O.G gauges, was considered necessary in order to avoid possible contamination by resuspended surface dust. The technical details relating to the instrument are given in section 4.2.

An exercise designed to test the performance characteristics of the Deposit Cannister has been carried out in which the measurement error and also laboratory analytical error have been investigated (described in Chapter 5).

1.5.4 Deposition surveys

Measurements of deposition rates were required as part of the investigation of spatial variability of heavy metal deposition and also as a basis for testing the source tracing methods used in this research. Ten metals were determined in samples of deposition; these were lead and cadmium and an additional eight elements copper, iron, magnesium, aluminium, chromium, zinc, manganese and arsenic. These additional metals were included as part of the source tracing method and also because they are of interest in their own right.

Two surveys of ambient deposition were carried out using the

Deposit Cannister. The first survey (Survey 1) was designed to provide a cross-section of industrial, urban, residential and rural environments on a 1km grid square pattern. The second survey (Survey 2) was designed to investigate the spatial variability of deposition at different spatial scales. In both surveys the exposure period was 30 days. Details of the sample frameworks used are given in section 4.3.

A third survey was conducted using a different sampling method; a flat snow-surface. This survey was designed to investigate the spatial distribution of 'hotspot' deposition around a prominent source. This survey was conducted to provide information of the fall out pattern downwind of a souce and is described in Appendix C.

1.5.5 Relating heavy metals in deposition to their component sources

The source analysis has been conducted in two stages. Firstly identification of the relative impact of sources of heavy metals in deposition was carried out using a Chemical Receptor Model. Secondly a simple source-based diffusion/deposition model was calibrated for iron foundry emissions to investigate the physical transfer process and also as a potential basis for further development of forecasting deposition from iron foundries.

The Chemical Receptor Model was based on Factor Analysis which aims to separate common variance in a large number of multi-elemental observations into a number of Factors. These Factors were taken to

evidence the influence of various source processes and were interpreted by matching the factor elemental profile against emission profiles from known sources. Cluster Analysis was then used to investigate the spatial associations between the factors and hypothesised sources.

The simple predictive diffusion/deposition model was based on a factor hypothesised to relate to iron foundry emissions. The model was used to predict factorscores rather than absolute concentrations of pollution and was based on an emission inventory for the iron foundry industry of Walsall. The model was used to predict how emissions eventually contribute to deposition both at the measurement sites and also at other areas of Walsall not involved in the deposition monitoring survey. Details of the model are given in section 7.4.

1.6 Broad conclusions and synopsis of the thesis

1.6.1 Introduction

In this section the essential findings of the research are summarised. A complete listing of the main conclusions and recommendations are given in Chapter 8.

The main outputs from the research are represented in figure 1.4 under the research objectives to which they relate. Each of these outputs or conclusions represents a contribution to current understanding of the heavy metal deposition problem.

1.6.2 Deposition Measurement

i) The Deposition Cannister has been specifically designed for use in large scale surveys of urban areas, having the advantages of easy siting and low cost. The measurement error of the Deposit Cannister is comparable to that of the standard deposit gauge methods. It has not been possible to compare the accuracy of the two methods because of time and resource constraints.

ii) The use of a snow-surface to collect deposition has also been tested. This method is particularly useful for detailed surveys of limited areas that may be of special interest but is obviously not a 'controlled' monitoring method.

iii) The deposit cannister method has been tested in a study involving upto 250 sample points which is the highest density of samples yet taken in a deposition survey in the United Kingdom. Losses were below 10%.

1.6.3 Spatial Variation of heavy metal deposition

iv) The statistical distribution of deposition of ten heavy metals has been found to be log-normal. Based on this distribution 0.3% and 4.0% of Walsall would be expected to exceed the F.D.R. maximum deposition standards for lead and cadmium respectively. The long term environmental health impact is potentially more significant for cadmium than for lead. Deposition levels of lead and cadmium fall within the expected range when compared to the limited evidence from other surveys of urban areas.

v) Spatial variations within a $1km^2$ ordnance survey grid square have been found to account for 67% and 63% respectively of the total variance of lead and cadmium deposition levels throughout Walsall. This considerable local variation is assumed to reflect the localised nature of fallout in the vicinity of sources and the micro-climatological variations in the meteorological factors controlling deposition (mainly wind velocity). This large spatial variation means that ideally many individual samples should be taken to obtain representative estimates of area deposition rates (a sample density representativeness relationship can be devised from this).

vi) The localised fall out pattern around industrial sources has been confirmed as being of the form of a exponential decay with distance from the source. This confirms that the bulk of deposition is confined to a 'hotspot' in the vicinity of sources and that maximum human exposure would therefore be expected to be similarly located.

1.6.4 Identification of sources of heavy metals in deposition

viii) The Chemical Receptor model of Factor Analysis has indicated that six source processes explain 88% of the variance of the observed deposition levels in Walsall. In order of decreasing importance these are crustal emissions (mainly coal and coke combustion), road and vehicle emissions, iron foundry emissions, copper refinery emissions, and two industrial general urban sources.

viii) Cluster Analysis has proved to be a useful technique for studying the spatial associations in deposition between different sampling sites. The advantage of using this technique is that it can identify sites which have similar deposition profiles and often these are associated with similar combinations of sources.

ix) An extension of the Factor Analysis has been to use factor scores as the dependant variable in a simple diffusion/deposition model. This allows the source modelling techniques to be applied in circumstances which would be otherwise impossible i.e. complex multi-source urban areas. This model has confirmed that the majority of deposition is largely confined to a limited radius around sources.

x) This research has contributed to the scientific understanding of the general processes involved in heavy metal pollution. The source identification techniques that have been developed in this research have important applications in pollution control policy, in that they allow environmental managers to compare the effects and effectiveness of different control strategies and devices, and so to improve the quality and effectiveness of pollution control.

1.6.5 Synopsis of the thesis

Having now established a general perspective to the research, the following Chapter 2 examines the current state of knowledge concerning the deposition of heavy metals. Chapter 3 then goes on to consider the source 'origins' of heavy metals and the various techniques that may be of value for identifying these sources. The research framework and experimental design are explained in Chapter 4. Chapter 5 contains the analysis of the results of the deposition monitoring exercises and the investigation into the performance of the deposit cannister. Chapter 6 details the analysis of the spatial variability of heavy metal deposition, the results of source identification exercise is described in Chapter 7 and the research conclusions are summarised in Chapter 8.

CHAPTER 2

DEPOSITION OF HEAVY METALS

2.1 Introduction to the purpose of the chapter

2.1.1 Summary

This chapter is a review of the general physical processes governing deposition of airborne material (fallout); the methods that have been developed for measuring it; and the general results that have been obtained for lead and cadmium in earlier and contemporary studies of deposition. In particular, this review focuses on the spatial pattern of deposition. The peak 'hotspots' of deposition found in urban areas are seen to present the most potentially significant problems for environmental health, whilst at the same time they are the most poorly researched aspect of deposition. This points to the need for research of the kind reported in this thesis.

2.1.2 Structure of the chapter

The deposition process incorporates three different deposition mechanisms. These are (a) sedimentation, (b) surface impaction, and (c) wet deposition. Each of these may vary in relative importance depending on the nature of emissions, distance downwind and certain meteorological factors. Section 2.2 examines the relative significance of these mechanisms to the overall problem of deposition in urban areas. Section 2.3 considers how the rate of deposition of metals may be measured and how the difficulties associated with the available measurement methods restrict the scale of ambient monitoring exercises.

Previous research into the levels of lead and cadmium deposition and the results obtained are reviewed in section 2.4 highlighting the spatial variability often observed in studies of deposition. The policy implications of deposition of heavy metals are explored in section 2.5.

2.2 The relative importance of different deposition mechanisms in urban areas

2.2.1 The physical characteristics of heavy metals in the atmosphere

Metals in the ambient atmosphere are present mainly in the form of suspended particles (some of the most volatile metals such as mercury and arsenic may be present as vapour, but the quantities concerned are not large and for the purpose of this research the phenomenon can be disregarded). The sizes and shapes of these particles vary extensively reflecting both the source features and the past history of the aerosols. Considerable attention is now being paid to these variations in shape and size because these physical attributes determine to a large extent, the atmospheric behaviour and subsequent health effects of the particles. There are however, difficulties in defining particle sizes simply and precisely. This problem is compounded by the many different particle sizing and sampling methods that have been used in the collection of data. Therefore, it is difficult to assess the significance of particular size distributions in terms of environmental health, and the available data should be treated with caution, particularly when cross-comparisons are being drawn.

Willeke and Whitby (1975) suggest that the size distribution for most aerosols is often multimodal. Bimodal and trimodal distributions have frequently been reported. These distributions are assumed to reflect the different mechanisms that contribute to the formation transformation and removal of atmospheric aerosols (Whitby, 1978).

When describing the particle size distribution of particular metal species, most authors use the Mass-Median Diameter (M.M.D)[1] to represent 'typical' particle size. In general the M.M.D for ambient aerosols containing lead and cadmium is in the micron-submicron range. Table 2.1 shows that M.M.D's in rural areas tend to be slightly smaller than in urban areas and are usually higher near to large sources.

Table 2.1 Mass-Median Diameters for suspended lead and cadmium particles

Location	M.M.D(μm)	Ref
Lead		
Chilton, Berkshire -	0.6	Cawse (1974)
Walker Branch Watershed, USA -	0.5	Lindberg et al (1981)
Cincinnati, Ohio -	0.2-0.4	Lee et al (1968)
Glasgow -	0.5	McDonald+Duncan (1980)
Swansea -	0.7	Pattenden (1974)
Steelworks, Kent -	0.7-1.0	Clayton (1981)
Leadsmelter, Missouri-	2.1-3.3	Dorn et al (1976)
Cadmium		
Walker Branch Watershed, USA -	1.5	Lindberg et al (1981)
Cincinnati, Ohio -	3.1	Lee et al (1968)
Glasgow -	0.6	McDonald+Duncan (1980)
Swansea -	0.7	Pattenden (1974)
Steelworks, Kent -	1.0-1.8	Clayton (1981)
Leadsmelter, Missouri-	1.1-2.1	Dorn et al (1976)

1 Mass-Median Diameter is the equivalent spherical diameter below which 50% of the total metal mass is found.

The particle size of atmospheric particles is an important factor governing the mechanism by which they are eventually removed by deposition. This section considers how the various deposition mechanisms may vary in importance in relation to the size of particle and also the meteorological factors affecting downwind dispersal of emissions from sources.

2.2.2 Deposition mechanisms

Deposition is the 'removal process' though which suspended atmospheric particulates are transfered to surfaces. The deposition process may take place through three possible mechanisms:

- sedimentation,
- surface impaction
- wet deposition.

Sedimentation is the more prominent mechanism for larger particles (generally $>5\ \mu m$) which have free falling speeds that exceed the net upward motion of air associated with vertical eddying. The lower size limit of particles that may be deposited by this mechanism is dependant on particle aerodynamic properties, wind velocity and turbulence.

Surface impaction is more prevalent for small particles ($<0.1\ \mu m$) due to the effects of molecular diffusion and is critically dependant on the nature of surfaces. It is predominently a lateral transfer process, in contrast to sedimentation which is largely a vertical deposition process. Rough surfaces present a larger surface area for impaction and may also capture small particles by filtration

effects (Hosker and Lindberg, 1982). The combination of sedimentation and surface impaction is widely referred to as dry deposition and can be expressed in terms of a deposition velocity, Vd[1]. Deposition velocity has been observed to be at a minimum for particles in the range 0.1 - 1.0 μm, and below this it is approximately a linear function of windspeed (McMahon and Denison, 1979). The relationship between Vd and particle size is shown in Figure 2.1. Particles greater than 1-10 μm are removed by sedimentation and surface impaction occuring at higher windspeeds. Particles below 0.1 μm are removed by diffusion impaction. Particles in the range of 0.1 - 1.0 μm tend to be removed by agglomeration and subsequent sedimentation or by wet deposition (Whitby, 1978). The effects of surface roughness, windspeed and particle form on deposition velocities have been investigated by several authors (eg Chamberlain, 1966, Clough, 1975, Little and Wiffen, 1977, and Davidson and Friedlander, 1978). However, these studies have been confined by practical difficulties to laboratory simulation or modelling exercises and consequently there is a generally poor understanding of particle behaviour in the environment (Hosker and Lindberg, 1982).

Wet deposition occurs in two modes: washout (below-cloud processes) and rainout (in-cloud 'scavenging'). In polluted urban areas washout is believed to be the dominant mode, whereas in rural areas rainout becomes the more common means of removing particles from the atmosphere (Muller and Beilke, 1977). Wet deposition by washout is most effective for particles in the 1.0-10 μm range while rainout mainly involves 'aitken nuclei', $<$ 0.1 μm diameter (Junge 1963).

---

1 Deposition velocity, Vd, is defined as the ratio of the net downward flux to the surface and the concentration of particles at a specified height.

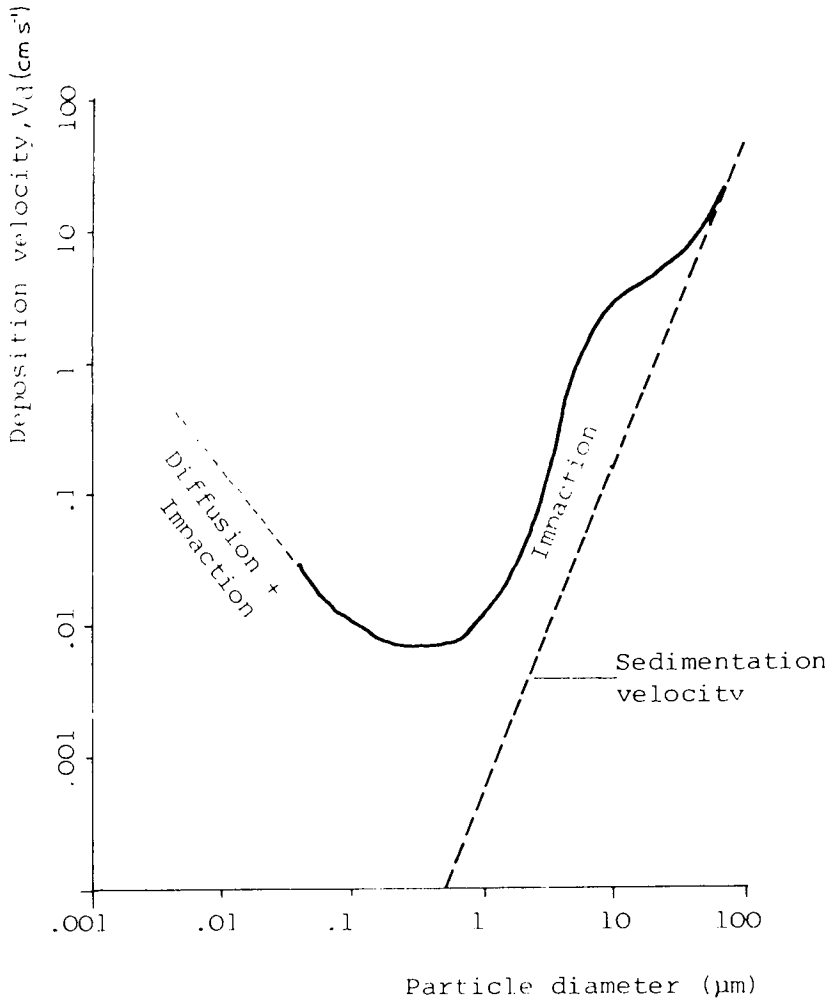


FIGURE 2.1 DEPOSITION VELOCITY VERSUS PARTICLE DIAMETER FOR A ROUGH SURFACE (based on work by Chamberlain, 1966 and Davidson and Friedlander, 1978).

Deposition is frequently measured as bulk deposition which includes both wet and dry fallouts. Measurements can be expressed either as a concentration of heavy metals in precipitation (mg/l) or preferentially as a fallout rate (usually $mg/m^2/30$ days). Results expressed as a concentration are of less use where total deposition inputs to the surface are being considered, but do have some use in evaluating the immediate health hazard involved in drinking rainwater (Galloway et al, 1980). The relative importance of wet and dry deposition can be assessed by measuring the two separately using automated collectors. Table 2.2 contains the results of surveys where the relative importance of those two deposition mechanisms have been compared.

These studies show that in rural areas wet deposition is generally the more dominant transfer pathway. In urban areas the relative importance of dry deposition increases. In the immedidate vicinity of large industrial sources the sedimentation of large particles can often result in dry deposition exceeding wet deposition as a removal mechanism (Pattenden and Branson, 1982).

The nature of source emissions, in terms of the particle size and density of emission, will be important factors governing how particles are deposited. Large dense dust particles, >10 μ m in size, will be rapidly deposited through sedimentation; while fine particles 1 μ m (typically metal fumes) will travel for greater distances downwind before being deposited.

Table 2.2 The relative importance of dry deposition of lead and cadmium

Location	$\frac{\text{dry deposition rate}}{\text{total deposition rate}} \times 100$	Ref.
Cadmium		
Wraymires, Cumbria	10%	Peirson et al (1973)
Tennessee	30%	Lindberg et al (1975)
German Cities	6-36%	Rohbock et al (1981)
Near Copper Refinery, Walsall	63%	Pattenden + Branson (1981)
Lead		
Wraymires, Cumbria	10%	Peirson et al (1973)
Tennessee	33%	Lindberg et al (1975)
Germany -Rural areas	4-8%	Rohbock et al (1981)
- Industrial/Urban areas	13-22%	"
Swansea, Clydach	51%	Pattenden (1974)
Near Copper Refinery, Walsall	83%	Pattenden and Branson (1982)

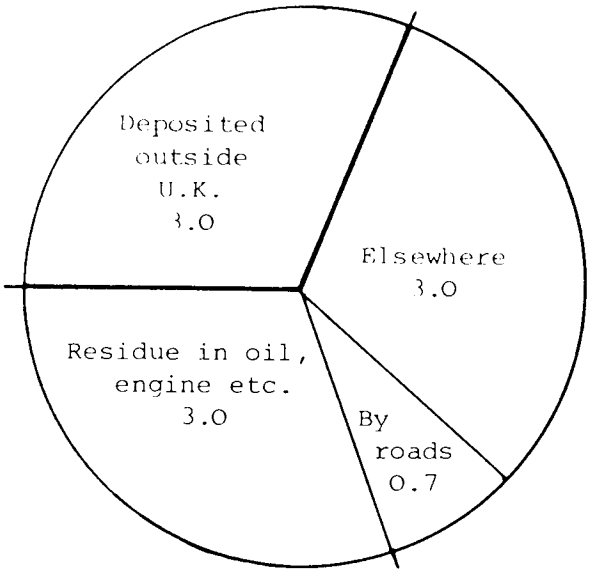


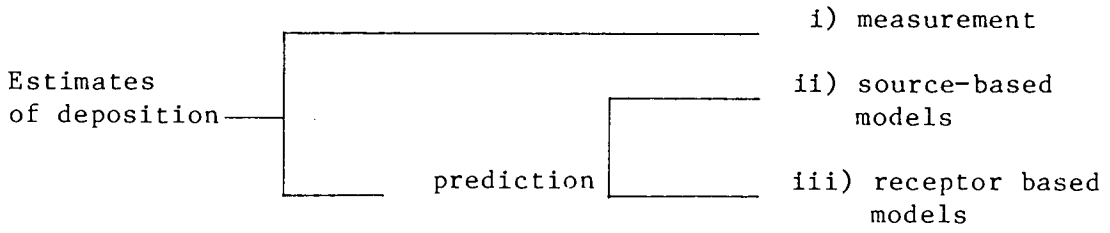
FIGURE 2.2 FATE OF LEAD ADDED TO PETROL IN THE U.K. IN 1981, thousand tonnes per year (source: Royal Commission on Environmental Pollution, 1983).

For example, lead emitted from petrol combustion in road vehicles is largely emitted as small particles below 0.3 μm (Little and Wiffen, 1977) which are subsequently transported over large distances. Figure 2.2 shows the estimated fate of 9700 tonnes of lead added to petrol in 1981. Only about 10% of the lead is emitted in large particles which deposit within 100 meters of a road; approximately 50% of emitted lead is blown out to sea. In section 2.4 the spatial distribution of heavy metals in deposition around industrial sources is examined in more detail.

2.3 Deposition measurement: review

2.3.1 Introduction

Estimates of deposition rates can be obtained in several ways:

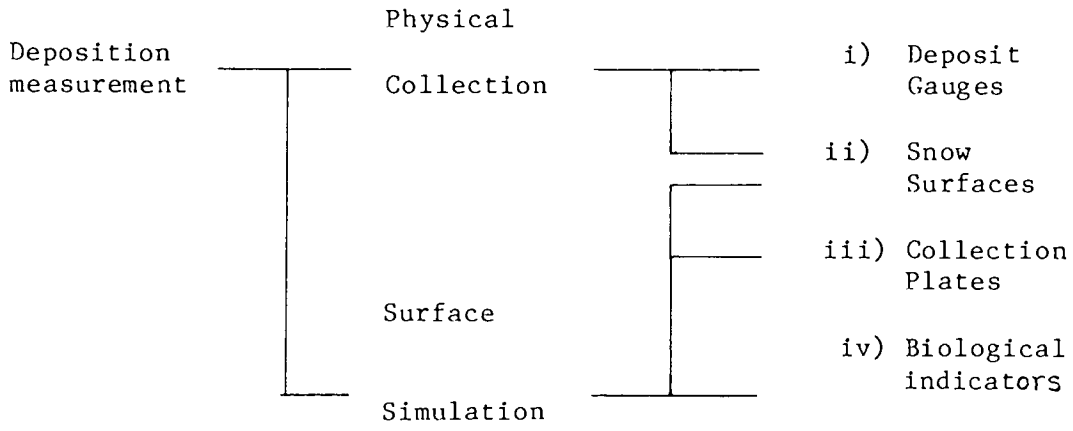


Deposition measurement involves either the physical sampling of falling particles, or collection of previously deposited material. However, practical and resource constraints limit the practicability of comprehensive measurement surveys. Consequently there is also a need to predict deposition, either for sites where measurements are not available or for the purposes of assessing the possible effects of changes in the controlling factors (eg meteorological conditions, and source emission rates) or of the effects of pollution control strategies. These predictive-based methods are considered in chapter 3. This chapter examines the existing measurement based techniques and in particular concentrates on the uses and limitations of these techniques in surveys of urban areas.

2.3.2 A summary of the currently available methods for measuring particulate deposition

The retention capacity of different surfaces varies widely and this can effect the net rate of metal input of deposited particles to the surface (Clough, 1975). Two basic deposition measurement strategies are therefore possible: firstly the downward flux of particles can be directly sampled or alternatively the net rate

of input of metals to a particular type of surface can be quantified. Using this basic division, a simple classification of measurement methods can be compiled:



Different measurement methods are appropriate for different types of surveys.

i) Deposit gauges

Deposit gauges aim to collect a representative sample of the deposition flux of particulate matter. From the discussion in section 2.2.2 it is evident that the vertical flux may consist of two types of deposition; wet deposition and sedimentation (a special type of 'CERL Directional' deposit gauge is available to sample the horizontal flux of particles by sedimentation and impaction, but this does not quantify the input of metals per unit of horizontal surface. This is described in British Standard 1747: Part 5, 1972). Horizontal deposit gauges collect vertically-moving particles and as such estimate the total rate of metal input to the ground surface over a period of time. These form the basis of all standardised measurement techniques (eg British Standard 1747:1, 1972, American National Standard, ASTM D1739-70 and International Standards Organisation, ISO/DIS 4222.2). Various other designs are used,

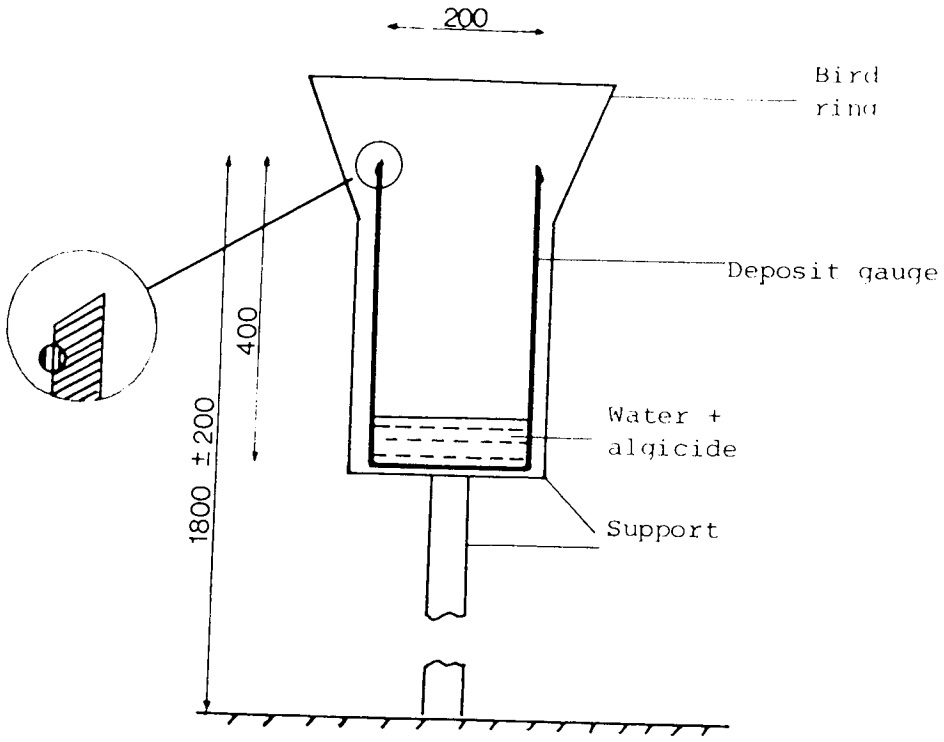
ranging in technical complexity from 'Jam Jars' (referenced in Duggan and Burton, 1983) to sophisticated wet/dry collectors (eg US Atomic Energy Commission Collector described by, Galloway and Likens, 1976). Design differences between the two standardised gauges currently employed in the UK (- the BSDG and ISO gauges -) are illustrated in Figure 2.3. The relative collection effeciency of these two deposit gauges is considered in 2.3.3.

The physical collection of deposition flux is the best method for estimating gross metal input to a horizontal area. However this method suffers from inherent disadvantages. The more precise and reliable standard gauges (International Standards Organisation gauge, ISOG, and the British Standard Deposit Gauge, BSDG) require secure siting in special frames, are bulky to handle and to analyse and are expensive to run and maintain. For these reasons, simple alternatives have been sought such as jam jars placed on window ledges; however the siting of these types of instruments is criticised (Hicks et al, 1980). This research project has succeeded in developing an effective instrument that overcomes these practical and siting difficulties (see Chapter 4).

ii) Snow-surfaces

Snow-surfaces have been used to collect gross deposition occuring by sedimentation, wet deposition and aerosol impaction in countries where snow fall is frequent (eg Forland and Gjessing, 1975 and Dovland and Eliassen, 1976). This method is a hybrid between physical collection of downward particle flux and net metal input to a particular surface. There is little likelihood of loss of previously deposited particles or of contamination by windblown

ISO DEPOSIT GAUGE



BS 1747 :1 DEPOSIT GAUGE

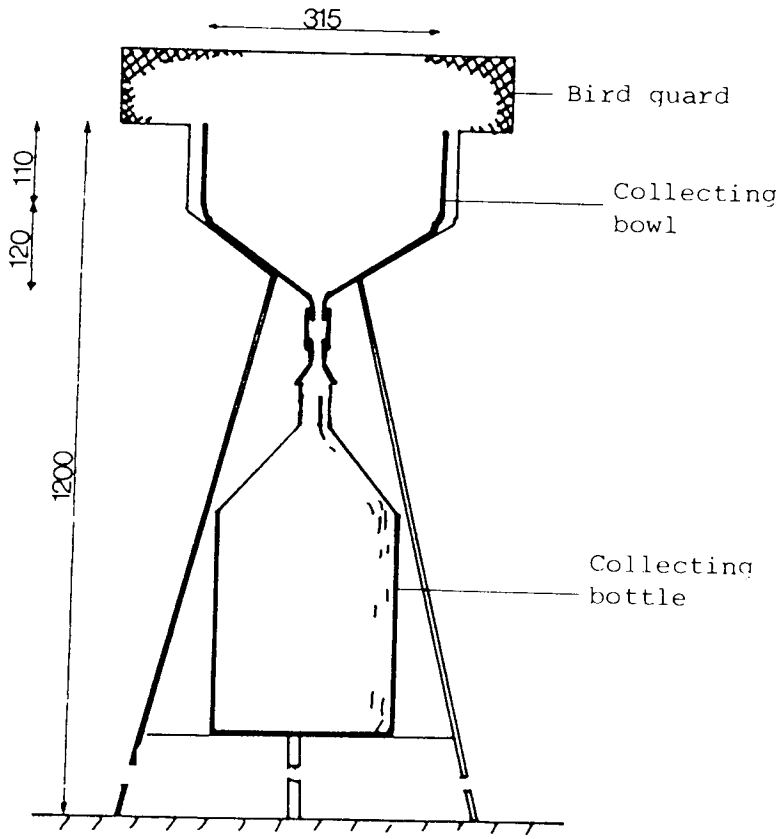


FIGURE 2.3 THE ISO AND BRITISH STANDARD DEPOSIT GAUGES.

surface dust. While this method is a useful alternative to deposit gauges, allowing large numbers of samples to be taken in an area, it is of course not directly controllable and has only limited application in temperate latitudes.

iii) Collection plates

These vary in form from simple petri-dishes to adhesive boards (Beaman and Kingsbury, 1982). All are designed as short term samplers that are only representative of net metal input to a particular surface. Examples of such surfaces range from highly-retentive sticky boards to low-retention white tiles. Their use in a quantitative capacity has been questioned (Hicks et al, 1980) because there is uncertainity about how reliably they represent the true deposition process.

iv) Biological indicators

Deposition of heavy metals to vegetation is interesting in its own right as it constitutes a potential route for human exposure (section 1.3.3) Natural vegetation may also be used as a deposition measurement method either by simply collecting samples of locally growing plants (eg Little and Martin, 1973 and Crump and Barlow, 1982) or by suspending samples of moss which are known to accumulate heavy metals (Clymo, 1963) in the technique known as the 'moss bag' (Goodman and Roberts, 1971). Moss bags collect sedimented, impacted and wet deposited particles. However, their retention capacity changes markedly according to the size and shape of the bag (Crump, 1980) and the moisture content of the moss (Clough, 1975) and as such they are only indicators of the input of deposition to similar

vegetation rather than being quantitative measures of the deposition flux.

It is clear that the last three methods (sticky surfaces, snow surfaces and biological materials), while providing useful techniques is certain circumstances, are not wholly appropriate for estimating the gross metal input to urban areas through vertical deposition fallout. Deposit gauges remain the only standardised method for measuring downward deposition flux, but the bulky nature and cost of standard BSDG and ISO types has severely limited the siting policy and the total number of sites that can be included in surveys, particularly in densely populated urban areas.

2.3.3. Issues relating to the collection characterisics and efficiency of deposit gauges

The BSDG (illustrated in Figure 2.3) has been widely used in the UK for ambient deposition monitoring. However, there have been criticisms of basic design, suggesting that in dry weather particles deposited in the collection funnel may be 'blown-out' by wind. Ralph and Barrett (1976) conducted a wind-tunnel investigation of the collection effi ciency of the BSDG and ISOG, and demonstrated that for large particles (120-970 μ m) blow-out occurs at windspeeds of 8-12 m/s in the BSDG. No blow-out was noted for the ISOG. In a field trial comparison however, Crossley and Hill (1982) found no significant difference to be detectable in long term means between the two types of gauge. They attribute this to frequent washing of the collecting bowl of the BSDG by rain.

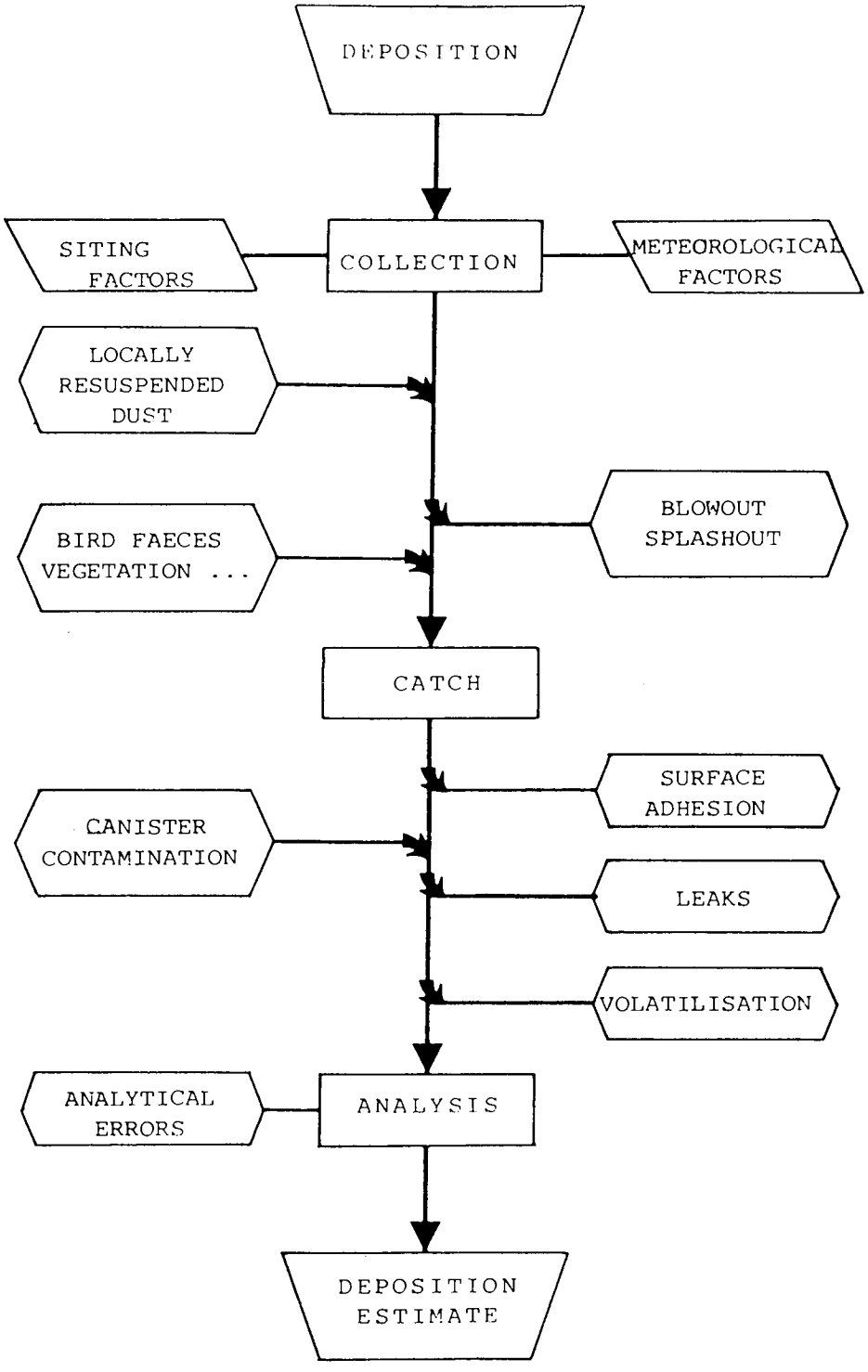


FIGURE 2.4 Diagrammatic representation of the problems involved in measuring deposition with a Deposit Gauge.

Crossley and Hill (1982) have also examined the replicability of the ISOG method using two identical gauges positioned together. The results of this comparison indicate that the measurement error of the individual gauge measurements was 0.282 $mg/m^2/30$ days (considered in more detail in section 5.2.3). Slanina et al (1979) have measured the precision of the BSDG using ten identical replicate gauges sited at a single location, monthly coefficients of variation (CV)[1] were in the range of 4-10% for lead and 6-37% for cadmium. The potential sources of error affecting the deposit gauge measurements are represented in Figure 2.4. Very little systematic investigation of the importance of these sources of error has been undertaken. However one interesting finding has shown that at high windspeeds the BSDG and ISOG do not capture large particles which are carried over the gauge by momentum (Ralph and Barrett, 1976).

Having viewed the available methods for measuring deposition, the discussion now moves to a review of comtemporary deposition surveys and their results.

---

1 Coefficient of variation is the relative variation:

$$C.V = \frac{\text{sample standard deviation}}{\text{sample mean}}$$

2.4 Contemporary Studies of Deposition

2.4.1 Introduction

The purpose of this section is to review the findings of previous monitoring surveys of deposition in remote, rural and urban areas, concentrating on lead and cadmium and to report the general levels of deposition rates that have been observed. Attention is also given to the empirical evidence for the distance-decline relationship. The studies reported are confined to those where standard 'deposit gauge' measurements have been used. A further point to note is the spatial variability in deposition rates.

Particles containing heavy metals are emitted by many of man's activities (these sources of emission are considered in detail in Chapter 3). These particles will be transported in the atmosphere downwind of sources; however, the rapid settling of larger particles and concentration dilution by dispersion of suspended particles suggest that deposition rates should decline with increasing distance downwind. In urban areas where there is a complex pattern of sources, one would expect deposition to be highly spatially variable, ranging from peak deposition levels in source 'hotspot' areas to near background in low density/open areas. In rural areas deposition is likely to be less spatially variable. These expected differences are illustrated in Figure 2.5.

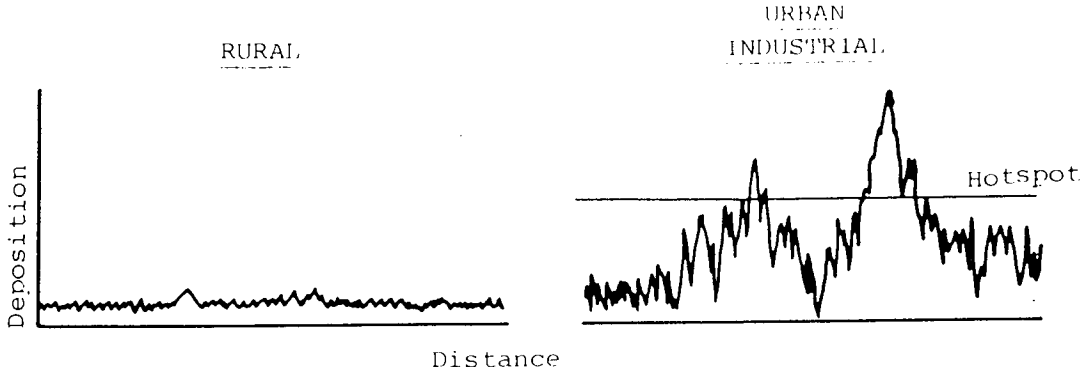


FIGURE 2.5 Illustration of the contrasting deposition profiles for rural and urban/industrial areas.

2.4.2 Lead and cadmium deposition rates measured in remote, rural and urban areas

Deposition rates for lead and cadmium measured at various urban, rural, and remote locations are summarised in table 2.3. Deposition rates for lead show a range of six orders of magnitude from 0.0001 $mg/m^2/30$ days in the remote Antartic to $>$ 100 $mg/m^2/30$ days near to large industrial sources. Deposition rates for cadmium show a range of five orders of magnitude from 0.00001 $mg/m^2/30$ days in the Antartic to >1 $mg/m^2/30$ days near industrial sources. However, there is evidence of considerable variability in the data for urban deposition rates; some levels are more typical of rural areas whilst others are substantially elevated. This supports the simple representation of distance decline and the relative spatial variability in urban and rural areas in Figure 2.5.

Table 2.3(a) Atmospheric deposition of lead at selected sites in contemporary studies

Location	Deposition ($mg/m^2/30d$)	Ref.
Remote		
Antarctica	1.0×10^{-4}	Boutron (1979)
Greenland	6.5×10^{-3}	Herron et al (1977)
Rural		
Scandinavian Glacier	0.35	Jaworoski et al (1975)
High Sierra, California	0.08	Hirao + Peterson (1974)
Nebraska	0.18	Struempler (1976)
New Hampshire	1.6	Schlesinger et al (1974)
Ardennes	0.69	Hallet el al (1982)
Western Michigan	0.8	Ter Haar et al (1967)
Wraymires, Cumbria	4.6	Peirson et al (1973)
Walker Branch Watershed	1.2	Lindberg et al (1981)
Chilton, Oxon - 1976	1.7	Cawse (1976)
Leiston, Suffolk	0.8	"
Styrrup, Notts.	1.7	"
Trebanos, Glam.	1.1	"
Wraymires, Cumbria	1.7	"
Urban		
New York and Chicago	8.3	Lazarus et al (1970)
Frankfurt, F.D.R.	2.7	Georgii et al (1984)
Hamburg	2.1	"
Essen	4.5	"
Deuselbach	1.2	"
Schleswig	1.5	"
London SW.7	6.8	Harrison et al (1975)
Hyde Park	3.6	"
London SE.2	5.7	"
Hounslow	3.8	"
Hounslow (air side)	2.6	"
Heathrow	4.1	"

Cont...

Charlshalton	2.5	Duggan and Burton (1983)
Kew, Cramorea	2.0	"
Kew, dusty area	4.0	"
Hampstead	5.0	"
Strand	7.0	"

Industrial Sources

1km from lead smelter, London	5.0	Duggan and Burton (1983)
500m from lead smelter, London	15.0	Duggan and Burton (1983)
1km from lead works, Leeds	7.8	Crossley and Hill (1982)
800m from lead smelter, U.S.A.	105.0	Dorn et al (1975)
85km from lead smelter, U.S.A.	8.2	"
10m from lead works, U.K.	50-250	Turner and Carroll (1980)
300m from lead works, U.K.	20-30	"
800m from lead works, U.K.	5-20	"
Near steelworks, Kent	6.0	Clayton (1981)
4.3km from lead smelter, Manitoba	3.5	Franzin et al (1979)
2.3km from lead smelter, Australia	3.0	Beavington (1977)
100m from lead smelter, Australia	39.0	"
Near lead smelter, Toronto	35-2334	Roberts et al (1976)
10m from lead mine	8.0	Johnson et al (1978)
250m from lead mine	2.8	"
Near copper refineries in Walsall	9-10	Cawse and Turner (1981)

Table 2.3(b) Atmospheric deposition of cadmium measured at selected sites in contemporary studies

Antarctica	1.9×10^{-4}	Boutron (1979)
Greenland	3.1×10^{-4}	Herron et al (1977)
Sub-arctic Finland	0.001	Laamanen referenced in Friberg, 1974

Cont...

Rural		
Nebraska	0.01	Struempler (1976)
New Hampshire	0.07	Schlesinger (1974)
Ardennes	0.11	Hallett et al (1982)
Walker Branch Watershed	0.04	Lindberg et al (1982)
Wraymires, Cumbria	0.21	Peirson et al (1973)
Various U.K sites	0.08	Cawse (1977)
Urban		
Various site in London	0.05 - 0.06	Duggan and Burton (1983)
Frankfurt, F.D.R	0.05	Rohbock et al (1981)
Hamburg	0.11	"
Essen	0.10	"
Deuselbach	0.02	"
Schleswig	0.04	"
77 cities in U.S.A		Hunt 1971, references
Residential areas	0.04	in Friberg et al
Commercial areas	0.06	(1974)
Industrial areas	0.07	
Industrial sources		
500m from lead smelter, London	0.09	Duggan and Burton (1983)
1km from lead smelter, London	0.10	"
800m from lead smelter, Missouri	4.3	Dorn et al (1975)
75km from lead smelter, Missouri	0.09	"
2km from smelter, Montana	1-4	Rupp et al (1978)
12km from smelter, Montana	0.04-0.19	"
4.3km from smelter, Monitoba	0.38	Franzin et al (1978)
2.3km from smelter, Australia	0.17	Beauington (1977)
100m from smelter, Australia	1.6	"

One interesting feature of the studies reported in table 2.3 is that in most cases very few measurements are taken, particularly in ambient urban area surveys. For example, Duggan and Burton (1983) used less than ten monitoring sites to represent the entire Greater London area. There have been no systematic investigations into the spatial representatives of individual deposition measurement sites in such areas. It is also interesting to note that many of the deposition surveys concentrate on measuring deposition in the vicinity of identifiable sources rather than surveying ambient urban areas.

Comparitively little monitoring has been undertaken for other heavy metals. The typical levels of deposition of the other metals included in this research are given in table 2.4. These indicate that there are large differences between remote areas and rural and urban areas, and yet even in urban areas, deposition levels more typical of rural areas can sometimes still be observed.

2.4.3 Spatial variation in deposition rates

It has already been stated that there is a distance-decline relationship in deposition rates, and that there are several factors governing the fallout process for airborne particulates, e.g. particle size, wind velocity, emission height and local topography. There have been many investigations into the pattern of metal contamination in a whole range of environmental media (not just deposition) around sources and the results of these studies generally show that metal contamination decreases with increasing distance from the source, in air (e.g. Turner et al, 1980; Roberts et al,

Table 2.4 Typical levels of Al, As, Cr, Cu, Fe, Mg, Mn and Zn deposition ($mg/m^2/30d$)

	Remote		Rural		Urban	
Al	0.001 - 0.05	2, 3	10 - 20	11, 12, 13	10 - 50	11
As	2.5×10^{-3}	6	0.03 - 0.2	11, 12	0.2 - 0.5	8, 11
Cr	-		0.2 - 4.0	3, 11, 12	0.2 - 2.0	4, 11
Cu	1×10^{-4} - 1×10^{-3}	2, 3	0.08 - 4.0	1, 3, 8, 9, 11, 12	0.1 - 65.0	4, 5, 10, 11
Fe	-		10 - 20	8, 11	15 - 150	4, 5, 7
Mg	-		-		20 - 50	5
Mn	0.05[5]		0.1 - 4.0	3, 11, 14	0.3 - 10	5, 11
2n	1×10^{-4}		0.1 - 15	3, 11, 12, 14	5 - 50	1, 4, 5, 10, 11

1) Anderson et al (1978)
2) Boutron (1979)
3) Cawse (1977)
4) Cawse and Turner (1981)
5) Duggan and Burton (1983)
6) Galloway et al (1980)
7) Georgii et al (1984)
8) Hallett et al (1982)
9) Herron et al (1977)
10) Lazarus et al (1970)
11) Pattenden (1974)
12) Pierson et al (1973)
13) Schlesinger et al (1974)
14) Struempler (1976)

1976), soil (e.g. Bachauer, 1973; Anderson et al, 1978 and Beavington, 1975), natural fauna and flora (e.g. Merry et al, 1981 and Little and Martin, 1972) and deposition (Turner et al, 1980; Vanderborought et al, 1983; Beavington, 1977; Roberts et al, 1976; Franzin et al, 1979; and Little and Martin, 1974). Lead deposition in the vicinity of roads has been observed to follow a similar decreasing trend with distance (e.g. Crump and Barlow, 1982 and Little and Wiffen, 1978). Cadmium deposition has also been noted to decline with distance away from roads (Lagerwerff and Specht, 1970). In many of these studies the form and the distance/decline has been noted to be a good approximation of an exponential decay. The nature of this distance decline relationship is illustrated in Figure 2.6 for several environmental media. In rural areas (2.6(b) and 2.6(c)) source impact can be detected at distances up to 30km from the source. However, in urban areas (2.6(a)), where there is a generally elevated and more spatial variable background level , the source impact attributable to an individual source becomes indistinguishable from the background at distances within a few kilometres radius of the source.

However, even in the close proximity of sources, levels at or near background can still be observed; thus the degree of spatial variability in deposition increases closer to sources.

The observed rapid distance-decline in deposition levels suggests that deposition of larger particles may be responsible for the 'peak' observed close to the works. Larger particles are frequently associated with fugitive emissions (uncontrolled emissions) rather than stack emissions which are generally of a finer size (e.g. Clayton, 1981).

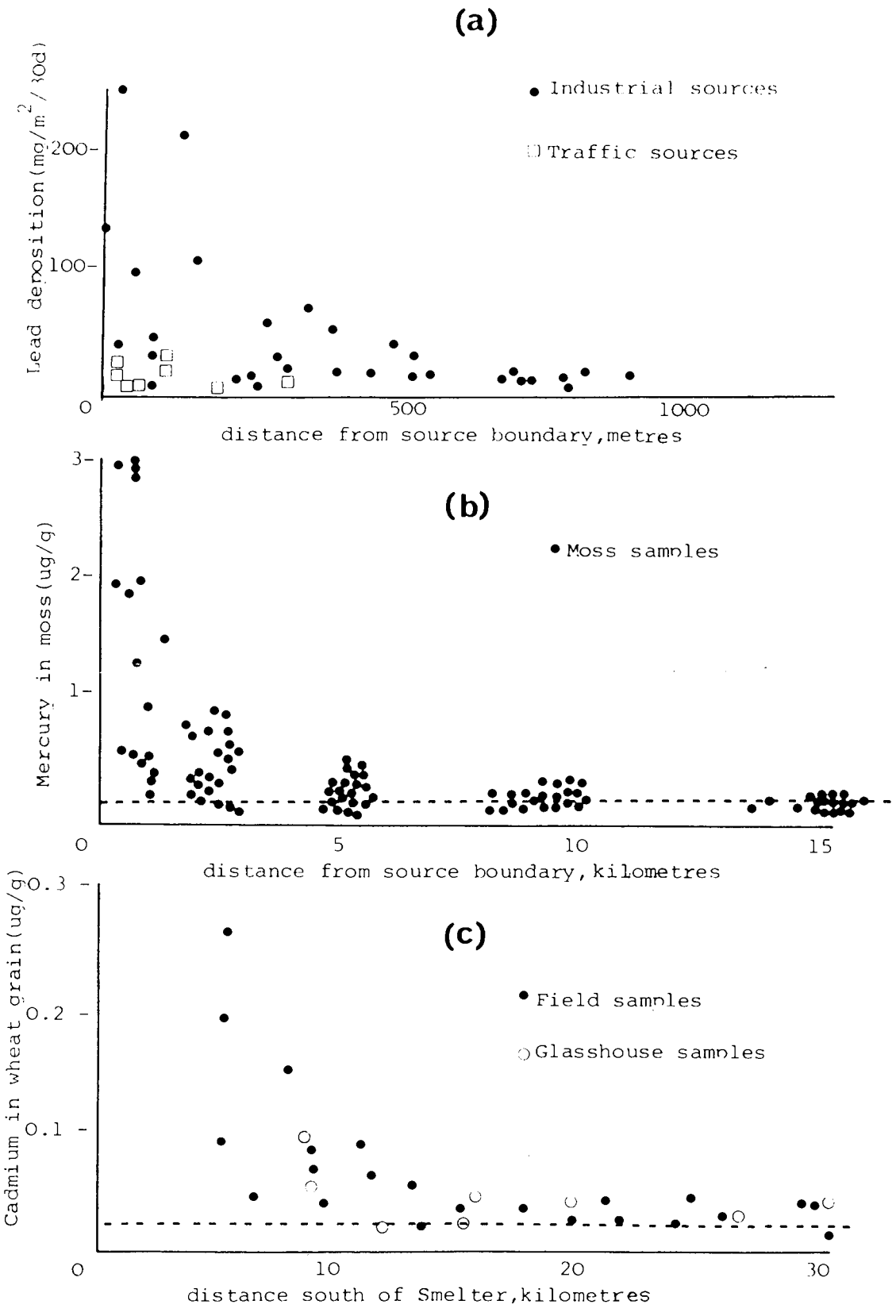


FIGURE 2.6 Dispersal of heavy metals around industrial sources. (a) Deposition of lead in the vicinity of lead works (Turner et al, 1980) (b) Mercury contamination of indigenous moss around Chlor-Alkali Plants (Wallin, 1976). (c) Cadmium in grain around a Lead-zinc Smelter (Merry et al, 1981).

2.4.4 Temporal variations in lead and cadmium deposition rates

Having considered variability in deposition rates over space, it is appropriate to consider briefly the variations in deposition rates occurring at a given site over time.

Pronounced seasonal variations in airborne concentrations of lead and cadmium have been observed at many locations. In Great Britain winter maxima are commonly observed (Salmon et al, 1978). These variations are attributed to the increased use of fossil fuels and the changes in meteorological factors governing the dispersion of airborne pollution. For deposition however, there is no clear relationship between deposition rates and the seasons of the year, deposition being strongly influenced by the discharges from localised sources which are frequently random or episodic in nature. For example, Pattenden and Branson (1982) have found no clear seasonal trend in deposition of lead and cadmium in the vicinity of a copper refinery in Walsall.

2.4.5 Surveys of metal deposition in the U.K

The above discussion covers international research, and for the purposes of this review it is useful to summarise the work that is currently or has recently been carried out specifically in the U.K.

There is no centrally co-ordinated network for monitoring heavy metal deposition in the U.K. that is equivalent to the National Survey of Smoke, SO_2 and airborne metals (McInnes, 1979). Some

individual local authorities carry out routine deposition monitoring but there is no standardisation in methods or siting policy and much of the information obtained is of limited value (Department of the Enviroment, 1974). The following surveys have been conducted, mainly to provide information on specific sources or issues:

i) Atomic Energy Authority of Harwell (AERE Harwell) have monitored deposition of a wide range of metals at seven sites in rural areas of the U.K. until 1977 and also maintain the rural background station at Wraymires, Cumbria.

ii) Warren Spring Laboratory have undertaken monitoring surveys in the vicinity of large industrial sources during investigations of specific localised problems (Turner et al, 1980 and Clayton, 1981).

iii) The Central Electricity Generating Board has monitored deposition in the vicinity of coal fired power stations near Selby (Green, 1982).

iv) A.E.R.E Harwell conducted a local survey of the Swansea area (Pattenden, 1974) following a previous study which had indicated high levels of local heavy metal contamination (Goodman and Roberts, 1971).

v) Deposition in the area surrounding the Avonmouth Zinc Smelter has been monitored using moss bags and some deposit gauges (Little and Martin, 1974).

vi) Deposition in the Greater London area has been surveyed in two separate studies (Harrison, 1975 and Duggan and Burton, 1983).

To conclude this review section, it is significant that there have been no systematic surveys designed to investigate the full extent and nature of spatial variation of deposition in ambient urban areas, although from studies conducted in the vicinity of sources it appears that deposition may be highly spatially variable over distances of even a few hundred metres. This brings into question the representativeness of large area surveys, which are forced by practical monitoring difficulties to rely on single gauge observations to characterise deposition occurring over wide areas.

This points to the need for future research in this area, and it is to this need that the research reported in this thesis in part responds;specifically in persuance of objectives Ob1 and Ob2.

2.5 Policy responses to the problem of heavy metal deposition

2.5.1 Deposition as an environmental health problem

Deposition of particulate matter may cause an environmental nuisance through deposited dust (Carey, 1959). But it is the chemical composition of deposited particles, in particular the presence of lead and cadmium, that is the basis of an environmental health hazard. This issue has already been reviewed in Chapter 1, where it was seen that deposition may act as a transfer route for contamination of other environmental media by heavy metals. Contamination of these other media may in turn present a direct threat to health. The most important of these transfer processes were seen to be:

- deposition onto food crops
- deposition to soil (and hence indirect contamination of crops)
- deposition to surface dust which may be ingested directly.

In order to avoid damage to human health through excessive uptake of toxic metals, particularly lead and cadmium, the levels of intake of these metals is controlled through statutory and advisory measures.

The following guidelines relate to these three important pathways:

i) Food

- Under the Lead in Food Regulations, 1979, the general limit for food intended for human consumption is 1mg/kg (fresh weight).

- No statutory limits on cadmium in food are laid down in the U.K. However, the Joint FAO/WHO Expert Committee on Food Additives have recommended a provisional tolerable weekly intake of 400 - 500 ug per adult (FAO/WHO, 1972).

ii) Soil

- There are no statutory limits for lead or cadmium in soil. The interdepartmental Committee on the Recla mation of of Contaminated Land (ICRCL 59/83) have recommended 'trigger' guideline levels for acceptable levels of metals for redevelopment of contaminated sites.
- The Department of the Environment (DOE) have recognised the problem of long term addition of metals in soil in sewage sludges in the form of guidelines for the maximum rate of addition to land (DOE and National Water Council, 1977).

iii) Dust

- Again there are no statutory limits on the lead and cadmium levels in dust but the Greater London Council have proposed a desirable safety limit for lead of 500 mg/kg (Duggan, 1980), and an 'action' level of 5000 mg/kg.

In addition to controlling human exposure via various intake pathways, there are also measures taken to control the lead and cadmium emissions at source, i.e. by controlling emissions. For example, there are controls limiting lead emissions from petrol (reviewed by the Royal Commission on Environmental Pollution, 1983) and from industrial processes (embodied under the Alkali and Works Regulations Act, 1906).

U.K. policy is therefore to control the potential public health problem from the airborne emission of heavy metals by a dual strategy of emissions controls and measures dealing with the levels of metals in the key 'intake' pathways of food, soil and dust. Deposition is an intermediate stage in the transfer process, and as such is not subject to maximum permissible limits of contamination. In the Federal German Republic (F.D.R.) however, the critical role of deposition in causing the addition of metals to the key 'intake' pathways has become recognised explicity in legislation (Weber 1981) setting 'action limits' on the deposition rates of lead and cadmium. This is outlined below.

2.5.2 Control Strategy for deposition in the Federal Republic of Germany

In the F.D.R., the concept of environmental quality standards ("immission" standards) is accepted as a basis for pollution control policy. Immission standards are designed to protect human health and the ecological capacity of the environment. If exceeded, an 'environmental quality maintenance programme' should be introduced to tackle the problem. Included in the Immission standards are limits on lead and cadmium deposition of 15 $mg/m^2/30$ days and 0.225 $mg/m^2/30$ days, respectively. Part of the overall legislative framework includes threshold levels for the protection of existing animals and plants of 7.5 $mg/m^2/30$ days for lead and 0.075 $mg/m^2/30$ days for cadmium (Weber, 1981).

In the U.K., environmental quality standards are gradually becoming embodied in the Government's pollution control strategy (e.g. the

EEC ambient air lead standards of 2.0 mg/m^3). However, there are no immediate proposals to extend the principle to deposition, but in this research the FDR approach is examined as a 'baseline' means of assessing the implications of any possible future move towards this approach to pollution control.

2.6 Conclusions relating to the deposition of lead and cadmium

2.6.1 Summary

This chapter has reviewed many aspects of the process of heavy metal deposition. From the perspective of this research, the main conclusions are:

i) The size distribution of suspended particulate matter is an important factor controlling the relative importance of various deposition mechanisms in removing particles to the surface. In general, the most important deposition mechanism is wet deposition, although the relative contribution of dry deposition increases in the vicinity of sources of metals to the atmosphere. Sedimentation is the most important mechanism in contributing to hotspots of deposition.

ii) Measurement of deposition can be achieved using a wide range of sampling devices but deposit gauges offer the most accurate and precise method for quantifying the total metal input to an area. However, there are many practical difficulties associated with the standard ISO and BSDG methods which limit the number of sites that can be surveyed in urban areas. These difficulties have in the past severely limited the scope of studies of ambient deposition in urban areas.

iii) From the previous and contemporary surveys of deposition it is clear that metal deposition rates are strongly affected by anthropogenic activity (in particular the industrial discharge of particulates to the air) and follow the general trend Remote<Rural<Urban. Deposition

'hotspot' areas may have levels of lead and cadmium deposition 5 or 6 orders of magnitude greater than remote regions of the world. The highest levels are found in the vicinity of industrial sources. For contemporary research, the number of deposition sample locations that have been used to characterise deposition in entire urban areas has been very small, with very low sampling densities. Given that deposition can show considerable spatial variation within an urban area, the representativeness of such surveys is questionable.

iv) Deposition follows an exponential decline with increasing distance from the source. Spatial variability is greatest near to sources. Even within a few hundred metres of large sources of metals deposition more typical of background levels may be observed. This has important implications for the design of surveys around sources suggesting that the greatest density of sample points should be close to the works.

v) While the principle of controlling metal accumulation in food, soil and dust is recognised in the U.K., deposition is not included under existing environmental quality guidelines.

In the following Chapter 3, the sources of heavy metals to the atmosphere are examined in detail, together with the methods for modelling explaining and predicting the spatial pattern of lead and cadmium deposition in complex multi-source urban areas.

CHAPTER 3

SOURCES OF HEAVY METAL EMISSIONS TO THE ATMOSPHERE IN URBAN AREAS AND METHODS OF ASSESSING THEIR CONTRIBUTION TO DEPOSITION RATES

3.1 Introduction

3.1.1 Overview

This chapter aims to explore the relationship between emissions of heavy metals to the atmosphere and observed levels and spatial distribution of metals in deposition. Specifically, it examines three important areas related to the third research objective, Ob.3, (1.4.4) which was to conduct source identification. These are; firstly, the controlling factors that govern the emission of heavy metals from sources; secondly, the methods that can be used to quantify heavy metal emission rates within urban areas; and thirdly, the transfer process linking environmental levels to their component sources and the ways that these can be modelled and used for the purposes of prediction and source identification.

3.1.2 Structure of the Chapter

The factors that govern emissions are extremely complex and very often our knowledge of emissions is limited to the most obvious industrial sources that can be easily identified. Section 3.2 examines these controlling factors and identifies the industrial processes with the greatest propensity to emit heavy metals. Section 3.3 examines the practical and technical difficulties associated with quantifying the emission rates of metals to the

air, and the ways that emissions data can be assembled and aggregated in the form of emission inventories. Section 3.4 reviews the field of 'source-related' atmospheric dispersion modelling. This is a tool often used to express scientific understanding of the relationship between emissions and environmental levels. Section 3.5 explores the field of 'receptor-based' modelling. This approach is an alternative to source-based modelling, and is useful in identifying sources of heavy metals, as observed in the environment, on the basis of unique identifying characteristics or 'finger prints'. The main findings and conclusions of the chapter ar given in Section 3.6

3.2 The Process of Heavy Metal Emission

3.2.1 Factors affecting source emissions

This section aims to examine the factors that may affect emissions of heavy metals to the atmosphere. Industrial processes are taken as the basis of this discussion because their direct contribution to the deposition of metals in urban areas forms the focus of interest in this thesis.

The generation of airborne particles containing heavy metals is a complex process. Two fundamental generation mechanisms can be identified; firstly the straight-forward mechanical suspension of particles containing heavy metals, and secondly the volatilization of metals at high temperatures. Mechanical suspension generally gives rise to solid particles which can be classified on the basis of their size (e.g. grit - $>75\,\mu m$ and dust 75 - $1\,\mu m$), form (e.g angular, smooth etc.) or density. Condensation of volatilized metal vapours gives rise to particles $<1\,\mu m$ in size known as metallurgical fume which generally consists of spherical chemospheres.

In addition to classifying individual particles it is possible to distinguish several modes of exit from the source i.e controlled (e.g stack discharges), uncontrolled (e.g escapes through roof louvres etc) fugitive or low level emissions.

If the industrial processes giving rise to metal emissions are represented in terms of a simple model, it is possible to identify which factors are most important in affecting emissions. This model is illustrated in figure 3.1 and from this it can be

seen that emissions will largely depend on the metal levels in raw material inputs, the nature of the industrial process and the effectiveness of pollution control devices. Of course in practice there are a great many other factors which can affect emissions for example the design and layout of installations, local meteorological conditions and plant management practice (Atkins and Lowe, 1979). All of these factors may vary both in time at a single plant and between different plants conducting the same operation. Variations in all of these factors will affect the total quanity of metal emission, its chemical state and particle size and form.

The picture is further complicated because at a single industrial site there may be large number of individual processes each giving rise to heavy metal emissions. If total emissions from the entire site are examined then it is clear that they will show large vaiations over time, and also in the way that they are dispersed to the environment.

3.2.2 Relative emissions capacity of different industrial activities

There is a wide variation in the quantity of heavy metal emissions from different industrial processes. This is partly due to the nature of the heavy metal emission process of a particular type of industry, and also due to variations in the scale of operations. There will also be variations in the mode of emission (e.g stack fugitive etc), emission height, particle size, chemical form and temperature. For this reason it is difficult to compare the significance of different types or forms of industrial emissions,

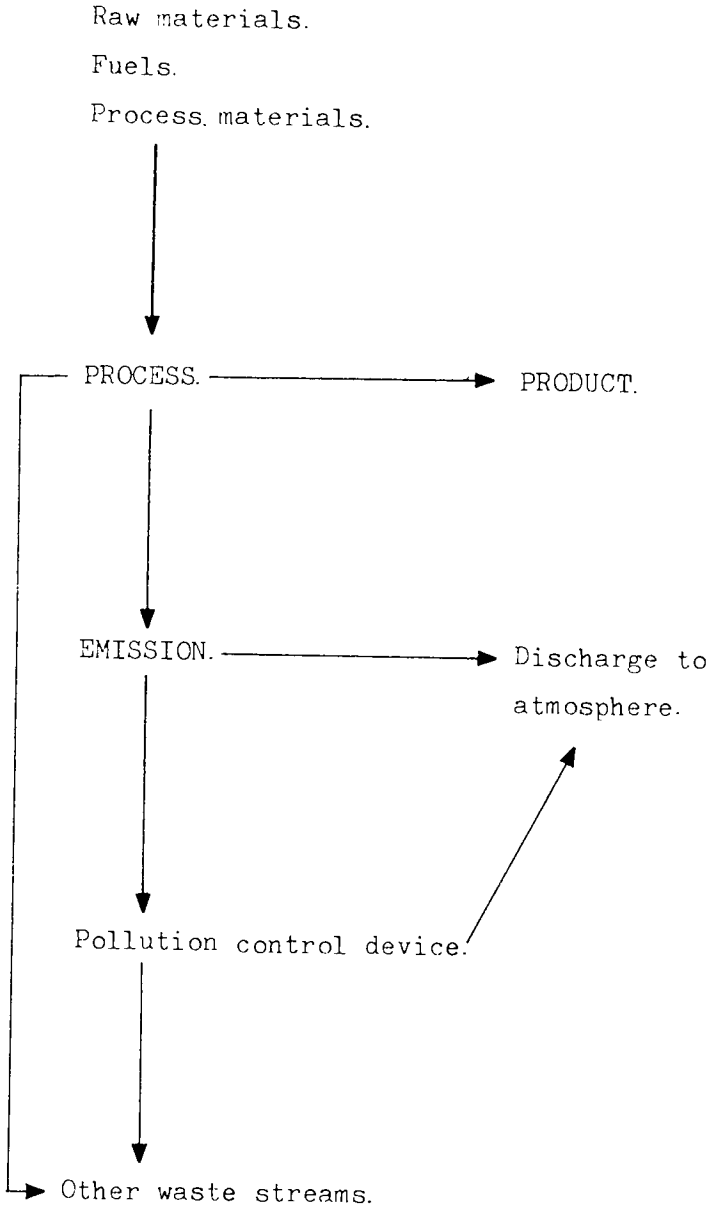


FIGURE 3,1 The Industrial Pollution Process.

(——→ metal transfer pathway.)

except at a general level. This is achieved here by qualitatively comparing industries using two criteria:-

- the toxicity of metals emitted,
- quantity emitted per typical plant.

Using these two criteria it is possible to identify certain groups of industrial activities which are potentially associated with significant heavy metal emissions. These are identified in Table 3.1 as industries rated with medium and high heavy metal pollution potentials.

Table 3.1 Heavy metal emission capacity of industrial groups in the U.K.

	Industries [1]	Relative Heavy metal emission potential
11	Agriculture and Livestock	Low
31	Food and Beverage Manufacturing	Low
321	Manufacture of textiles	Low
323	Manufacture of Leather	Low
33	Manufacture of Wood and Wood Products	Low
34	Manufacture of pulp, paper and paperboard	Low
35	Manufactured of Industrial Chemicals	Medium
354	Manufacture of Petrolum and coal products	Low
355	Manufacture of Rubber Products	Low
36	Non-metallic Mineral Industry	Medium
37	Basic metal industry	High
38	Manufacture of fabricated metal products, machinery and equipmment	Medium
41	Electricity and Gas production	Medium

1 Indexes to the standard industrial classification Codes of all Economic Activities, Statistical paper, series M, No. 4, 2 ad 1, U.N. Statistical Office, New York

The manufacture of industrial chemicals may involve processes which manufacture metal based chemicals or use metals as catalyts or process materials. The non-metallic mineral industry frequently involves generation of metal containing dusts, or high temperature emissions of volatile metals. The basic metal industry involves a wide range of processes in which metals are melted, refined and smelted all of which may lead to fume emissions. In the U.K the predominance of the secondary metal industry means that metal emissions are highly dependant of the contamination of scrap metal (Tunnicliffe 1973 and Mantle, 1973). Metal fabrication and equipment manufacturing may include welding, dropforging, grinding and heat treatment of metals. The generation of electricity by coal combustion is associated with metal emissions from the metals in coal.

This comparison has been made at the industry level, clearly there are a wide variety of actual activities in each industry which may be associated with metal emissions. In Table 3.2 these activities are listed and a ranking given to their potential emissions. This ranking is based on a qualitative consideration of the two criteria given previously and is applied to a 'typical' site for each activity. Table 3.2 also indicates which of these activities are scheduled under the Alkali & C. Works Regulations Act, 1906. These are mainly non-ferrous and ferrous processes and are under the statutory control of the Industrial Air Pollution Inspectorate (IAPI). As such they are governed by the criterion of Best Practicable Means. This basically means that emissions are controlled to satisfy specified 'presumptive limit' emission standards. Two processes having relatively high heavy metal pollution potentials are not

included under the Alkali & C Regulations Act, 1906; these are the ironfoundry Cold blast cupola (Fellowship of Engineering 1981) and metal recovery in scrap yards (Brookfield, 1983).

As well as industrial emissions to the atmosphere there are certain non-industrial processes that may emit metals in urban areas, these include transportation (particularly lead from petrol), domestic coal combustion (Commission ofthe European Communities, 1980) waste incineration and incineration of sewage sludge (Greenberg et al, 1981 and Bennett and Knapp, 1982). Metals may also be derived from resuspension of urban dust and soil. However it is difficult to comment on the relative importance of these sources because very little research has been conducted in this particular area.

Table 3.2 Industrial Activities and Processes which have an airborne heavy metal pollution potential

Activity and typical metal emissions	Relative 1 Pollution Potential	Scheduled Works ☆
Manufacture of Pulp & Paper		
Pulp Production (Hg)	C	
Paper Production (Ti,Zn)	C	
Manufacture of Industrial Chemical		
Basic Inorganic Chemicals		
Phosphate Fertilizers (Cd)	B	
Sodium Hydroxide (Castner-Kellner Process) (Hg)	C	☆
Chlorine manufacture (Hg) (Chlor alkali)	A	☆
Paints, Varnishes and Pigments (As, Ba, Cd, Co, Pb, Mn, Se, Ti, Zn)	B	
Pesticides (As)	C	
Explosives (Hg)	C	
Organic Chemicals		
Synthetic rubber, Plastics and Fibres (Cd)	C	
Soap by Fatty Acids (Zn)	C	
Lubricant oil re-refining (Zn, Ba, Pb etc)	C	
Antiknock (Pb)	C	
Dyestuffs (Cr, Se)	C	
Metal Mining		
Non-Ferrous metals	B	

Activity and typical Metal emissions	Relative Pollution Potential	Scheduled Works ☆
Non-Metallic Mineral Industry		
Glass and Glass products (As Ba, Mn, Pb, Se)	C	
Basic Metal Industry		
Iron and Steel		
Metallurgical Coke Oven (As,Zn etc)	C	☆
Blast Furnace (Cr,Cu,Mn,Ni,Pb,Zn)	A	☆
Basic Oxygen Furnace (")	B	☆
Open Heath Furnace (")	B	☆
Electric Arc Furnace (")	B	☆
Ironfoundry (Hot-blast cupola) (any)	A	☆
Ironfoundry (Cold-blast cupola) (any)	A	
Ironfoundry (Electric Melting) (any)	C	
Steel Foundry (any)	A	☆
Ferroalloy production (Cr, Mn)	A	☆
Non-Ferrous Metals		
Primary Aluminium (Al)	B	☆
Secondary Aluminium (Al,Zn,)	B	☆

Activity and typical Metal emissions	Relative Pollution Potential	Scheduled Works ☆
Primary Copper from Blister (Zn,Pb Ca)	A	☆
Secondary Copper Refining (As Cd,Cu,Sn,Pb,Ag,Zn)	A	☆
Brass and Bronze Foundry (Zn,Pb Cu)	B	
Lead Smelting (As,Cd,Zn,Pb)	A	☆
Secondary lead smelting (Pb, Cu,Sn,Sb,Zn)	A	☆
Lead foundry (Pb)	B	
Primary Zinc Smelting (As, Cd, Sn, Sb, Pb, Zn)	A	☆
Secondary Zinc refining (Zn, Pb, Cd)	B	☆
Arsenic Works (As)	A	☆
Beryllium Works (Be)	B	☆
Selenium Works (Se)	A	☆
Chromium Works (Cr)	B	☆
Cadmium casting (Cd)	A	☆
Manganese Works	B	☆
Tin Smelting (As,Sb)	B	☆
<u>Metal Recovery</u>		
Cable burning (Zn,Pb,Cd)	A	☆
Scrap metal recovery (any)	C-A	

Activity and typical Metal emissions	Relative Pollution Potential	Scheduled Works ☆
Manufacture of Fabricated Metal products, machinery and equipment		
Chromium Plating (Cr)	C	
Nickel Plating (Ni)	C	
Galvanizing (Zn, Pb)	C	
Welding Cutting etc	B	
Electricity, Gas and Stream Production		
Coal and oil Power Plants (V,Cr,Pb Hg, Zn, Cu, Ni)	B	☆

1 Qualitative ranking

A, potential to emit either a large quantity of metals and or highly toxic metals

B, medium potential metal emission

C, specific metal problem usually minimized in practice

3.3 Area-based emission inventories

3.3.1 Obtaining estimates of emissions within urban areas

This section examines the problem of estimating how much heavy metal is being emitted to the atmosphere within predefined geographic areas. In most urban/industrial areas, such as Walsall, there is a multiplicity of different industrial and non-industrial sources varying both in activity and emission rates. Some of these sources are identifiable as specific points (mainly individual factory sources) while others are 'line or'area' sources such as vehicle traffic and domestic coal combustion. The process of identifying and quantifying these emissions is a cruical part of the understanding of the nature of heavy metal pollution process (section 1.3), and provides a basis for comparing the relative importance of different sources within an area and also as the starting point for modelling the transfer process linking source to receptor.

3.3.2 Methods for quantifying industrial emission rates

A crucial stage in determining the effects of emissions on the environment is being able to obtain estimates of the rate of emission. Such estimates can be obtained either at an individual level (ie for each factory or works), or at a level of spatial aggregation (the area-based or collective approach). There are two basic alternative methods by which these estimates can be obtained;

- measurement of individual emissions,
- applying emission coefficients to known and identified sources.

Measurement usually involves physically collecting samples of emission by inserting a sampling probe (eg BCURA probe) into the effleunt gas stream. There are a number of standardised source sampling procedures (eg American Society for Testing and Materials, ASTM D-2928-71, part 23 and British Standard, B.S. 3405-1971). The B.S. 3405 provides for within-stack sampling of particulates of larger than 1 μm with an expected accuracy of $\pm$ 25%.

There are however several technical and practical difficulties which may affect the accuracy and representativeness of stack sampling:

- Sampling errors may occur if the sample probe is not sampling isokinetically[1] and dust flow around the probe may be affected by the physical presence of the probe itself (Vincent et al, 1982). It is often difficult to achieve isokinetic conditions in a stack where flow rate is turbulent and constantly changing (Perry and Young, 1977)

- Practical sampling problems may stem from the nature of the hostile chimney environment. In practice, B.S 3405 is difficult to achieve and grab samples are frequently taken (non-isokinetic short-term samples).

- The representativeness of a single short period measurement for estimating long term emissions is questionable, particularly when the variations in emissions may show wide differences even over the short-term (Warda and Buhr, 1973).

---

1 Isokinetic means that the sample face intake velocity matches the streamline flow within the stack.

As well as the 'controlled' emissions discharge from chimney stacks, there are further industrial emissions that are uncontrolled (usually termed 'fugitive emissions') from roof louvres, external sources and mechanical action. Emissions in this form cannot yet be reliably measured and quantified although research is in progress to tackle this problem (Wallin, 1983, personal communication). Emissions may also be estimated by using 'Emission Coefficients'. These coefficients relate the quantity of an emission to an index of industrial production rate such as output, firm size or raw material consumption. They can be based either on previous monitoring surveys or on estimates of emissions based on input/output calculations and have the advantage over measurement in that they are very flexible and may be adjusted to account for pollution control efficiency, production changes and even fugitive emissions (Orleman, 1983). Emission coefficients are preferable for estimating emissions from individual sources because of the greater uncertainties surrounding a single source measurement, since one measurement can only be related to the specific conditions prevailing at the time of sampling (Goklany, 1980), whereas emission coefficients are usually based on an extensive series of tests or calculations. However, the greatest value of emission factors is that they are easy to apply in the process of aggregating the estimates of emission from a number of similar sources within an inventory area. They are also useful for estimating emissions from 'area' and'line' sources from which 'homogenous' emissions are assumed. Typical examples of emission coefficients are given by Little and Wiffen (1978) relating the quantity of lead emitted along a road to the lead content of petrol and the speed and number of vehicles; figures of 8-10 mg/metre/sec are cited for 1000 vehicles per hour on a typical U.K road.

Emissions coefficients do however suffer from certain difficulties. These are:

- Emission coefficients are only widely available for the common macropollutants such as SO_2 and total particulates (Vandefrift et al, 1977 and Environmental Protection Agency, 1977) and the more widely studied micropollutants such as lead (Nriagu, 1978 and Davies et al, 1973),

- The accuracy of an emission coefficient is most directly related to the number of studies performed on particular sources. In general, the most intensive efforts are usually concentrated on the major pollutants. They are also only as accurate as the original measurements upon which they are based,

- Coefficients based on studies of a limited number of plants may not be representative of all industrial processes. They are most valid when applied to an industry as a whole. When applied to individual plants there may be significant differences between the predicted and actual emissions.

However, even when these limitations are taken into account, emissions coefficients can be extremely useful in establishing emission inventories, particularly at the urban scale where the large number and variety of sources makes sampling impractical.

3.3.3 Compiling an emission inventory

An emission inventory is a set of data on the emissions of a particular pollutant within a given geographical area. In order to compile an inventory, information is required for each source or source groups (aggregate data), on the following items:

- emission rates and or production/comsumption rates,
- type, characteristics of emission and particle size,
- pollution control efficiency,
- discharge times and duration,
- location.

The objectives of the inventory will determine the degree of resolution and aggregation required of this primary data. A comprehensive inventory may be used as the basis of dispersion modelling exercises and may include very detailed information, while less detailed inventories may only deal with total emissions in certain areas, presented as yearly averages (Committee on the Challenges of Modern Society, 1978).

There may be problems in identifying all sources in an area. The most obvious industrial sources are usually identified from local knowledge or from data obtained from national trade bodies. Smaller sources may have to be identified from site inspections or from secondary information sources such as telephone directories, local trade organisations etc. Questionnaire or telephone surveys may then be conducted to obtain the required information on production processes etc. (World Health Organisation, 1982).

TABLE 3.3 Emission inventories for Worldwide and EEC emissions of Lead and Cadmium to the atmosphere,(t/y). (Sources: Pacyna,1984 and Nriagu,1979)

	LEAD		CADMIUM	
	World *	EEC ×	World *	EEC ×
Conventional thermal power plants	14000	1138	60	101
Industrial/residential fuel combustion	—	1652	—	155
Wood combustion	4500	562	200	25
Gasoline combustion	273000	74300	3	31
Mining	8200	1090	2	1
Primary non-Ferrous Metals:-				
Copper/Nickel	29500	9250	1600	595
Zinc/Cadmium	16000	7880	2910	1550
Lead	31000	10450	200	8
Secondary non-ferrous Metals:-				
Copper	770	55	600	6
Zinc		—		—
Lead		387		1
Iron & Steel,Ferroalloy	50000	14660	70	58
Refuse incineration	8900	804	1400	84
Phosphate fertilizer	50	6	210	27
Cement production	—	746	—	15
Industrial applications	7400	—	50	—
Misc.	5900	—	—	—
Total	449220	122980	7305	2653

* Data for 1975 × Data for 1979

— No data.

3.3.4 Applications of emissions inventories

The reason for compiling emission inventories will determine their scale and resolution. A global inventory may be used to compile what are termed metal 'budgets' (Nriagi, 1979). National or regional inventories may be used as policy tools (Benkitz, 1982 and Cass and McRae, 1983). Local inventories may be used for air quality management schemes, sample survey design and dispersion modelling (eg Ball and Bernard, 1978). As an illustrative example, Table 3.3 contains inventories of lead and cadmium emissions at a global and E.E.C scale. This type of emission-accounting has a valuable national policy role. However, this example also illustrates one of the difficulties of inventories. Cadmuim emission in certain categories at the E.E.C scale apparently exceed world-wide emissions. This demonstrates how errors may occur both in compiling data and applying emission coefficients.

Where inventories are compiled as part of an Air Quality Management system, they play a positive role in helping to direct control where it is needed to comply with Immission Standards. Nato (1978) have reviewed the air pollution management strategies of six member counties who use inventories as an essential part of national control policy. In the U.K, where pollution control is essentially source based (using the 'Best Practicable Means' criteria) there are no national inventories and the only ones that have been compiled are used for local planning and control purposes (eg Ball and Bernard, 1978). There are no examples of detailed inventories of heavy metal emissions in the U.K.

The compilation of an emission inventory for the Ironfoundry industry in the Walsall/West Midlands area is described in Appendix A.

3.4 Atmosheric dispersion and deposition modelling

3.4.1 Introduction

As was stated in the introduction to this chapter, one means of identifying the contribution of an air pollution emission to the levels of pollution found in the environment is through 'source-based' prediction models, usually termed dispersion or diffusion models. This section of the chapter reviews the availability, form and usefulness of some models and assesses the extent to which they can be applied in the context of deposition.

Source-based models aim to model mathematically the physical transfer process that takes place subsequent to the airborne emission of substances to the environment, taking account of factors which may influence environmental levels, such as variations in emissions and the dispersive properties of the atmosphere. The alternative 'receptor' type of model, seeks only to identify sources. The contrasting roles of these two types of model are illustrated in Figure 3.2. The role of receptor models is considered in Section 3.5.

3.4.2 The basic types of source model

The field of source modelling has grown around the prediction of gaseous dispersion from idealised point sources. Many of the published models are of theoretical rather than practical value. The three main types of model are:

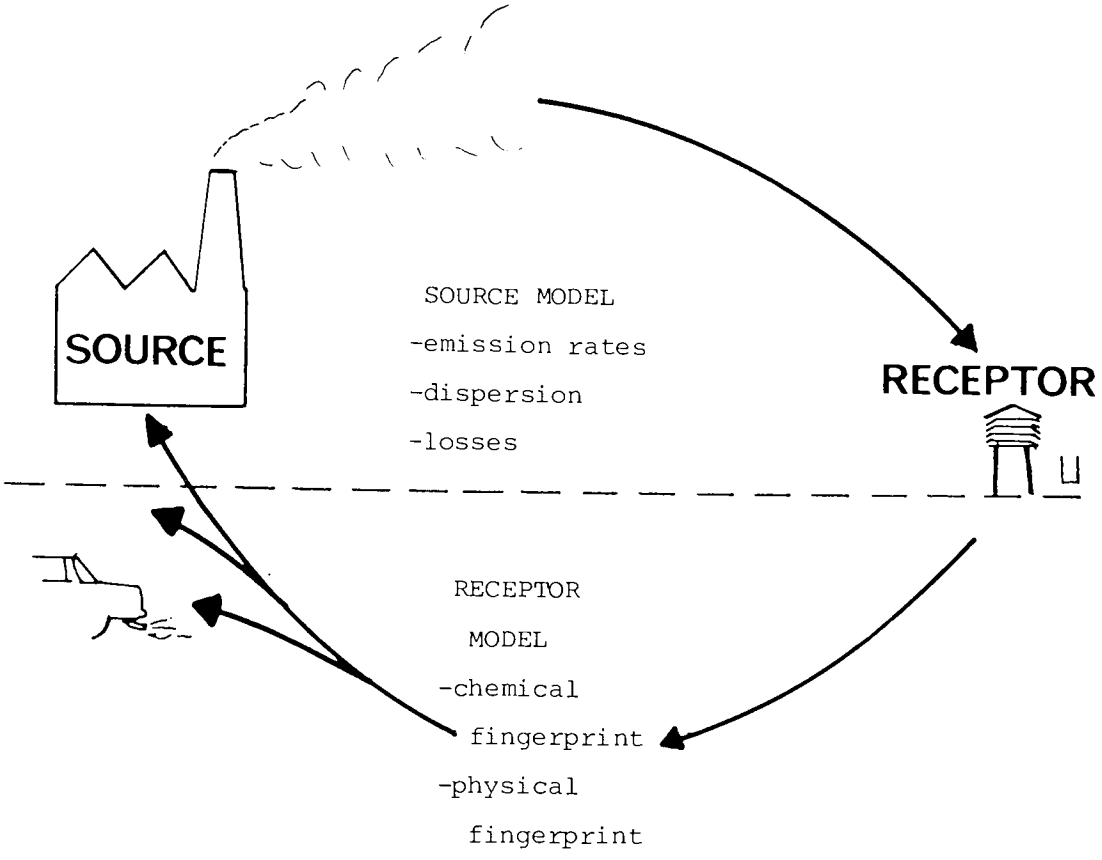


FIGURE 3.2 The roles of Source models and Receptor models.

- input/output models (or 'box' models)
- deterministic diffusion models (the 'gaussian' plume models)
- statistical models

Input/output models or box models aim to estimate airborne concentration within a conceptual box of given dimensions and limited vertically by mixing height. Gifford and Hanna (1971 and 1973) have proposed a number of box models based on the basic area proportionality model:

$$X = C \cdot Q/U$$

where X is concentration, Q is source strength within the 'box' area and U is windspeed. The parameter C is a weak function of city size (usually about 225 for particles). More complicated box models divide the city into smaller areas and solve balance equations between each box and may also account for cross wind transfer (e.g. Sharma, 1976). These types of model are simple to operate and in practice may be of comparable accuracy to more sophisticated models (Turner et al, 1972).

Deterministic diffusion models are of two types, Lagrangian and Eulerian. Langrangian models, such as the Gaussian Plume Model, are based on moving co-ordinate systems. Eulerian models such as the k-theory of atmospheric dispersion, are based on fixed locations without recognition of the history of an air mass at a specified point in space. Both are ideally applied to single sources in flat terrain but have been extensively modified to include line and area sources (Turner, 1979). The practical problems of predicting urban area pollution are dealt with by integrating the distributions from individual sources (Calder, 1977). However, those models then

require high speed computing and vast amounts of complex meteorological data making their use prohibitive except at the research scale. Statistical models are used for forecasting pollution using multivariate techniques such as multiple regression (Auwera, 1977) but are of limited practical value.

2.4.3 Deposition models

The theoretical basis for predicting ambient air pollution of gaseous macropollutants such as SO_2 has been well established; by contrast the field of particle deposition has been received comparatively little attention. Deposition is considered in some dispersion models as a removal process from the atmosphere, but only in so far as it allows the remaining airborne concentration to be calculated. For example, the simple source-depletion model (Corbett, 1981) and the more sophisticated surface-depletion model (Horst, 1977) have both been proposed to take account of deposition by surface absorption from a Gaussion Plume. The surface depletion model has been extended to include the K-theory of diffusion (Berkowicz and Prahm, 1978). Peterson (1978) has included a removal term in a simple box model. The source depletion Gaussion model has been tested by Vanderbrought et al (1983) in the vicinity of an industrial source where deposition was predicted with an accuracy of better than 60%.

Wet deposition around point sources has been considered by Rodhe (1980) to follow an exponential type of decay with distance. Rodhe proposed three types of model based on the general relation:

$$d(r) = \frac{Q \times \Phi(r)}{2 \prod r}$$

where d(r) is deposition per unit area per unit time, Q is a constant emission rate (kg/s), r is distance from source and $\Phi(r)$ is a frequency function which gives the amount deposited per unit distance. For the first model (1) $\Phi(r)$ is given by an exponential markov or distribution of dry and wet periods, the shape of d(r) is shown in Figure 3.3. The second model assumes $\Phi(r)$ to have a simple exponential decay with distance and has two forms, (2a) is a simple distance decay, and (2b) is a variant where the fraction of time that particles experience precipitation is taken into account. The third model (3) assumes that what is emitted during precipitation remains inside the precipitation area during travel. The results of all models are shown in Figure 3.3. Model 1 is taken as the most realistic, model 2a seriously underestimates deposition for distances less than 50km, 2b overestimates and model 3 is very good approximation out to about 20km but underpredicts past this distance.

In an equivalent manner, dry deposition by sedimentation is considered by Bosanquet (1950) to be a function of particle free falling speed, f, emission height, H, and horizontal wind velocity V:

$$\text{Average rate of deposition } (g/m^2/\text{month}) = \frac{3.27 \times Wb \times 10^4}{H^2} \times F\left(\frac{f}{v}, \frac{x}{H}\right)$$

where W is rate of dust emission in gms, b is the fraction of time during which wind is in the direction of a 45° segment and x is distance from the source in ft. Values of the function $F\left(\frac{f}{v}, \frac{x}{H}\right)$ are given from curves given in their original paper. The downwind deposition pattern of particles will critically depend on their

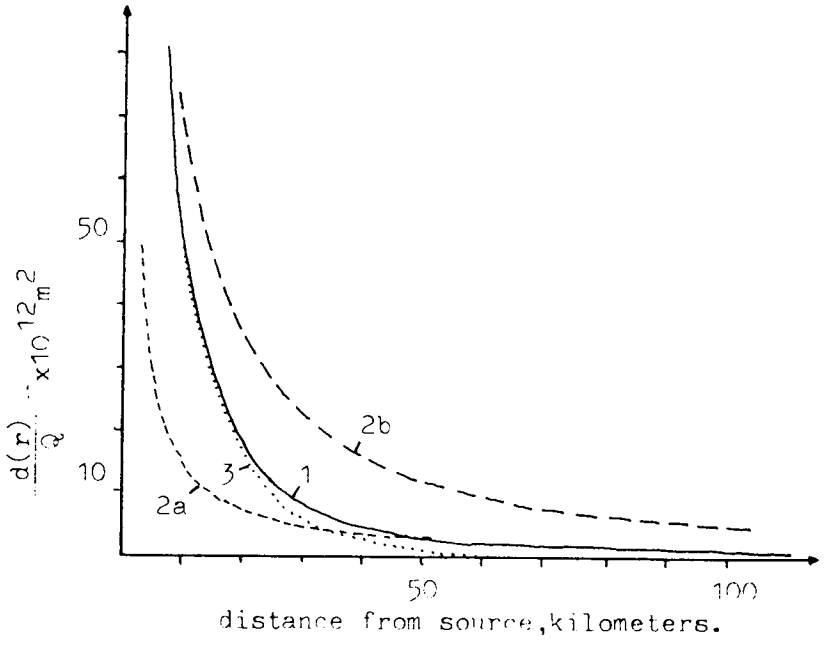


FIGURE 3.3 Normalised wet deposition as a funtion of distance from the source for the three models proposed by Rodhe(1980).

density and size (i.e. free falling speed). Figure 3.4 shows the downwind deposition pattern of particles emitted from a 375 ft stack emitting 30 gms of dust with specific gravity of 2 in light wind conditions of 5ft/s. The form of the distance decline is in rough agreement with that observed around actual sources (described as a distance decline function in section 2.4)

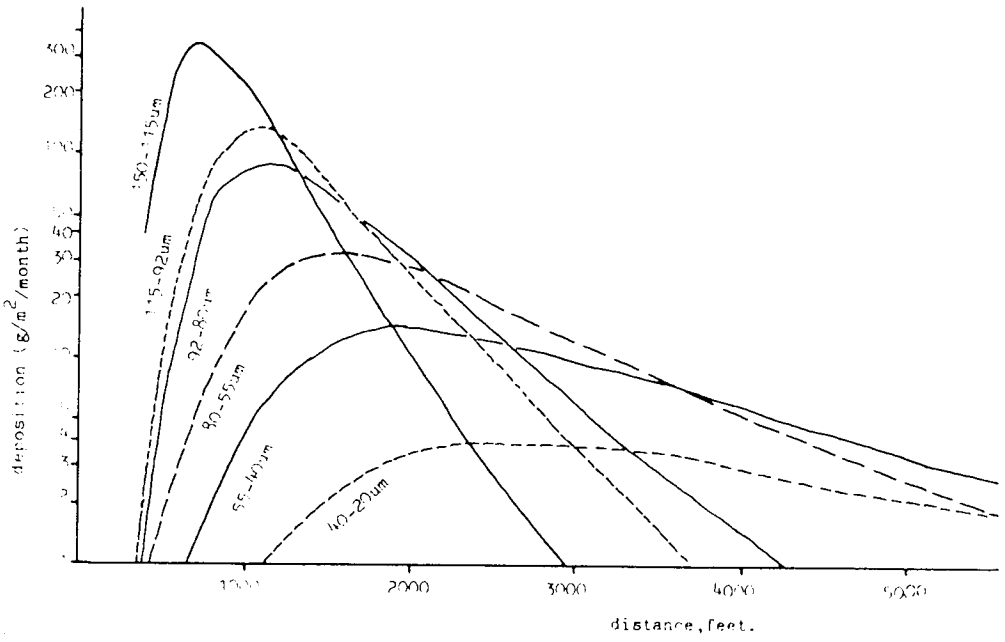


FIGURE 3.4 Deposition pattern of dust downwind from a source at a wind speed of 5ft/s (source:Perry and Young,1977).

None of these deposition models has been applied to heavy metal deposition in complex urban areas where the multiplicity of minor sources, many of which are not easily identified or emission rates quantified, means that calibration against observed environmental levels is technically extremely difficult to carry out. The difficulties and inaccuracies in obtaining reliable emission data act to further weaken the validity of such models in urban situations.

For these reasons there has been a general rejection of the source-based model in the case of heavy metals in urban areas, particularly for deposition. Instead, receptor models have been widely developed as a way of identifying which sources and source-types contribute to the urban problem of heavy metal contamination. These models are reviewed in section 3.5.

3.5 Receptor Models

3.5.1 Introduction

The development of receptor models has originated in the United States of America as a response to the need to be able to identify the sources or origins of the heavy metals found in the urban atmosphere, in order to comply with Air Quality Management Standards (Cooper and Watson, 1980). For the reasons described in the preceding section, source-based models have been unable to satisfy this need and instead receptor models have been widely adopted as a principal 'source identification' technique.

This section describes the field and receptor modelling, concentrating on the receptor models that are most suitable for adaptation to the identification of sources of heavy metals in deposition (Ob.3).

3.5.2 Principal methods of source identification

Receptor models are based on the concept that pollutants measured at a receptor (usually an ambient air monitoring station) will show certain unique characteristics that derive from their origin. These unique characteristics can either be physical characteristics such as particle morphology (Mc Crone, 1967 Bradley et al 1981) and electromagnetic/density properties (Perry and Young, 1977) or chemical characteristics such as the presence of tracer substances (substance emitted from a unique source) or a characteristic pattern ('fingerprint') of interelemental ratios between component elements (Hopke et al, 1976). The physical characteristics technique is restricted in application to larger particles such as those present

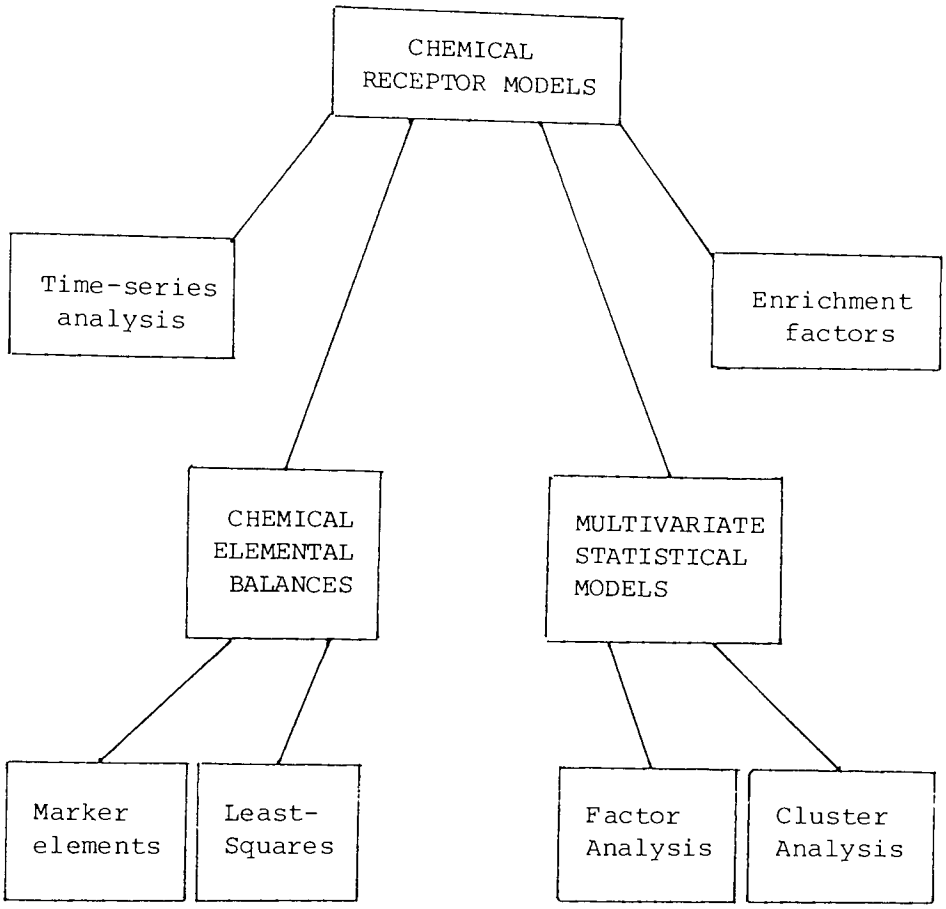


FIGURE 3.5 Classification of Chemical Receptor Models.

in road-dusts (Linton et al, 1977). Chemical charateristics are more generally useful for identification of sources in air pollutants and, as will be seen, in deposition.

There are four types of chemical receptor model, these are identified in Figure 3.5. Of these, only two are used to identify unique sources of particles; these are chemical elemental balances (ceb) and multivariate analysis. These will now be discussed in turn.

(a) Multivariate analysis

Multivariate methods, such as factor analysis and cluster analysis (pattern recognition), extract information about sources on the basis of inter-elemental variability found in a data set derived from a large number of samples. They have the advantage that no apriori assumptions regarding sources are required. The assumption is made that if two or more elements originate from the same source or source-type, their variability over time or space will be similar. The 'modelling' methods aim to detect this common variability and allow the source to be inferred (Hopke et al, 1976).

Cluster analysis presents the spatial correlation matrix in more easily-understood graphical form, allowing source identity to be inferred from the common variance of elements of particular clusters. Factor analysis aims to express the correlation matrix as a linear combination of factors which may be associated with their sources by comparing interelemental profiles (Blifford and Meeker, 1967). Both models assume that all major source influences are reflected in the correlation matrix. This assumption may not be valid if sources give a homogenous spatial background or temporal

TABLE 3.4 Examples of commonly derived factors and their elemental profiles.

Authors	FACTORS (hypothesised interpretation)								
	General Urban	Fuel oil	Vehicle Exhaust	Crustal Sources	Marine	Cement Dust	Iron & Steel	Refuse Incineration	Unidentified
Mc Innes (1979)	Fe,Mn,Zn, Cu,Pb	Be,Ni,V							
Linton et al (1977)			Pb,Zn,Mn, Br,Fe,Co, Cd	Ce,Hf,Zn, Co,Na,F					Fe,Co,Cd, Mn,Cr,Pb
Boutron & Lorious (1979)	Pb,Cd,Cu, Zn,Ag			Al,Fe,Mn, K,Ca	Na,Mg				
Gatz (1978)			Pb,Br	Al,Ti,Si, K		Ca	Fe,Mn		
Hopke et al (1976)		V,Cr	Br	Al,Fe,Sc, Th,Mn	Na,Cl			Zn,Sb	
Gaarenstrome (1977)	Cd,Zn,Ni, Cu,Pb,Li, Mn,Ni,Cr, Na		Br	Na,K,Fe, Ca,Mg,Rb, Sr,Al,Ti, Al,Ti,Ni,					NH_4,SO_2, Cu,Ni,Zn, Pb,NO_3
Blifford & Meeker (1967)		Fe,Cu,Sn	Pb,HC's				Fe,Mn,Ti		

consistency. Correct interpretation may be affected if source factors are spatially autocorrelated or have chemically similar profiles. As an example of how these factors are interpreted, table 3.4 present the results of previous factor models contrasting the elements that are taken to be associated with different sources; for example automobile exhaust is frequently associated with a factor loaded on lead and bromine both of which may be emitted from petrol combustion.

(b) Chemical elemental balances (CEB's)

Chemical elemental balances are based on chemical fingerprints for all major sources. These are made up of interelemental ratios and marker or tracer elements. According to the CEB method, proposed by Miller et al (1972), the atmospheric concentration of an element, Ci, is a linear combination of particles from many sources, each weighted by a source strength term, Mj:

$$Ci = \sum_{j} Mj.Xij$$

This approach suffers the major disadvantage that sources must be characterised accurately (i.e. there emission profiles must be known). For the same reasons that make source models unreliable in urban areas (e.g. measurement and source identification difficulties) solutions obtained from this method may often be incomplete (Gordon, 1980).

3.5.3 Applications of receptor modelling

Developments in the field of receptor modelling have been made largely in connection with air pollution studies. Blifford and Meeker (1967) established the first multivariate model for cities throughout the U.S.A. Miller et al (1972) used a simple tracer/marker approach to develop the chemical elemental balance method. Since these pioneering studies a great number of receptor models have been applied to identify sources of heavy metals in the atmosphere using multivariate methods (e.g. Hopke et al 1976, Gaarenstroom et al, 1977, Gatz, 1978, McInnes, 1979 and Heidam, 1984), and chemical elemental balances (e.g. Friedlander, 1973; Gatz, 1975; Gartell and Friedlander, 1975, Ozubay, 1980 and Cass and McRae, 1983). The factor analysis model has been successfully extended to source identification in urban road dust (Linton et al, 1977 and Hopke et al, 1980) and snow (Boutron and Lorious, 1979).

Receptor models, particularly those based on multivariate methods such as Factor Analysis can, conceptually at least, be used to identify sources in any environmental media, providing that account is made of any selective addition or removal processes which may alter interelemental ratios between source and receptor.

3.5.4 A comparative assessment of source and receptor models in terms of their usefulness for this research

The third objective of this research is centred around explaining the relationship between sources and levels of heavy metals in deposition. This chapter has presented a number of basic tools that can be used to study the relative importance of different

TABLE 3.5 Comparative assessment of Source and Receptor Models.

Features	Source Model	Receptor Model
Source data	-detailed emission rates required -sources must be located	-no emission rates -need not be known
Elements	-special models for volatile or reactive species -single elements can be measured	-stable particles only -multielemental data required
Purpose	-prediction	-explanation
Calibration	-large data set on environmental levels & meteorological conditions	-inherent
Resolution	-depends on model inventory and atmospheric data	-depends on the accuracy of analytical procedures
Policy Use	-policy evaluation -pollution alerts -air quality plans	-source indentification

sources that contribute to environmental levels in urban areas. The source based diffusion/deposition models have been shown to be not widely used in such situations because of the difficulties in identifying all sources of heavy metals and obtaining estimates of emission rates. In response to this deficiency, receptor models have been developed as an explanatory tool for explaining levels in terms of source contributions. However, receptor models have not been developed as predictive tools and they cannot be used to study the nature of the pollution process linking sources to receptor. In table 3.5 the contrasting roles of these two models is highlighted.

Core et al (1981 and 1982) have recognised that receptor models are not exclusive alternatives to source models, and that a strategy of joint application can be beneficial. These authors have used a receptor model to identify sources more accurately and so complete an emission of the traditionally difficult sources such as domestic wood burning and fugitive dusts. In this way they capitalise on the best features of both models: the receptor model's power of explanation and the source model's capacity for prediction.

Although neither source based models or receptor based models have been applied to the problem of studying heavy metal deposition in urban areas, they are both flexible enough to be adapted for this role. For this reason this research has developed and applied a multivariate receptor model and a source-based deposition model for use in urban areas. For the receptor model, a dual strategy comprising factor analysis and cluster analysis has been used because for these models no a priori assumptions regarding the number and nature of sources need to be made. The application of

both source based and receptor models to the problem of identifying sources of heavy metals in deposition in Walsall is described in chapter 7.

3.6 Conclusions

3.6.1 The nature of the emission process

The interaction between emissions to the atmosphere and environmental levels of heavy metals is extremely complex. This chapter has outlined the basic tools that may be employed to study these interactions. This section details the broad conclusions of this chapter.

Emissions are a complex function of many controlling factors and show wide variations over time and between different sources. The main industrial sources of heavy metal emissions to the atmosphere are those connected with metal melting, smelting and refining operations where process materials are heated above the melting points of many of the more volatile and toxic heavy metals.

3.6.2 Quantifying heavy metal emissions

The practical and technical problems associated with physical sampling of emissions from each individual source have meant that in most cases 'emission coefficients' may be aggregated at different spatial levels to form an 'emission inventory'. These may comprise a simple statement of total emissions within a predefined area, or a complex breakdown of emissions by type of source and location of each individual emission. Inventories may be used as air pollution management tools or as the basis for mathematical prediction models. However, they have not been widely used in the U.K because pollution policy is directed towards control at source, rather than 'emissions control' using environmental quality standards.

3.6.3 Modelling the dispersion/deposition of emissions

The field of source based dispersion modelling has not developed to the point where it can be exclusively relied upon to tackle the problems associated with heavy metal deposition in urban areas. Problems with identifying and quantifying emissions together with problems associated with calibration have meant that in this context source-based techniques have for the most part been superceded by receptor-based models. These are of great value for identifying sources; however they are of little value in studying the nature of the dispersion process and the changes that may occur over time resulting from changes in emissions and control policies. This research has therefore taken both types of model; specifically a source-based deposition model has been calibrated for emissions based on a chemical receptor model of factor analysis and cluster analysis. This approach is specifically designed as a practical method for conducting 'source identification' in a complex, multi-source urban areas, therefore responding to the research objectives set out in Ob.3. The method is spelt out in more detail in the following Chapter 4, which deals with the research method and experimental design.

CHAPTER 4

RESEARCH FRAMEWORK AND EXPERIMENTAL DESIGN

4.1 Research Methodology

4.1.1 Summary

This chapter describes the research method that has been adopted to satisfy the three research objectives; viz. Ob.1 deposition measurement; Ob.2 - spatial levels and variation; and Ob.3 - source identification. There are two strands to the research method: firstly the basic elements of practical 'experimentation', which include:

- the design and testing of a new deposition measurement instrument, and the associated analytical procedures,
- a 'case study' investigation using the new deposition measurement instrument in a field survey of deposition in an urban area to provide basic data on deposition,
- the investigation of 'hotspot' deposition using the snow-surface monitoring method,

and secondly elements of 'theoretical' development:

- a systematic structured analysis of spatial variation in deposition rates,
- the source tracing method based on the multivariate receptor models of Factor and Cluster Analysis,
- the prediction of deposition rates using a source-based deposition model calibrated using the results of the Factor Analsyis.

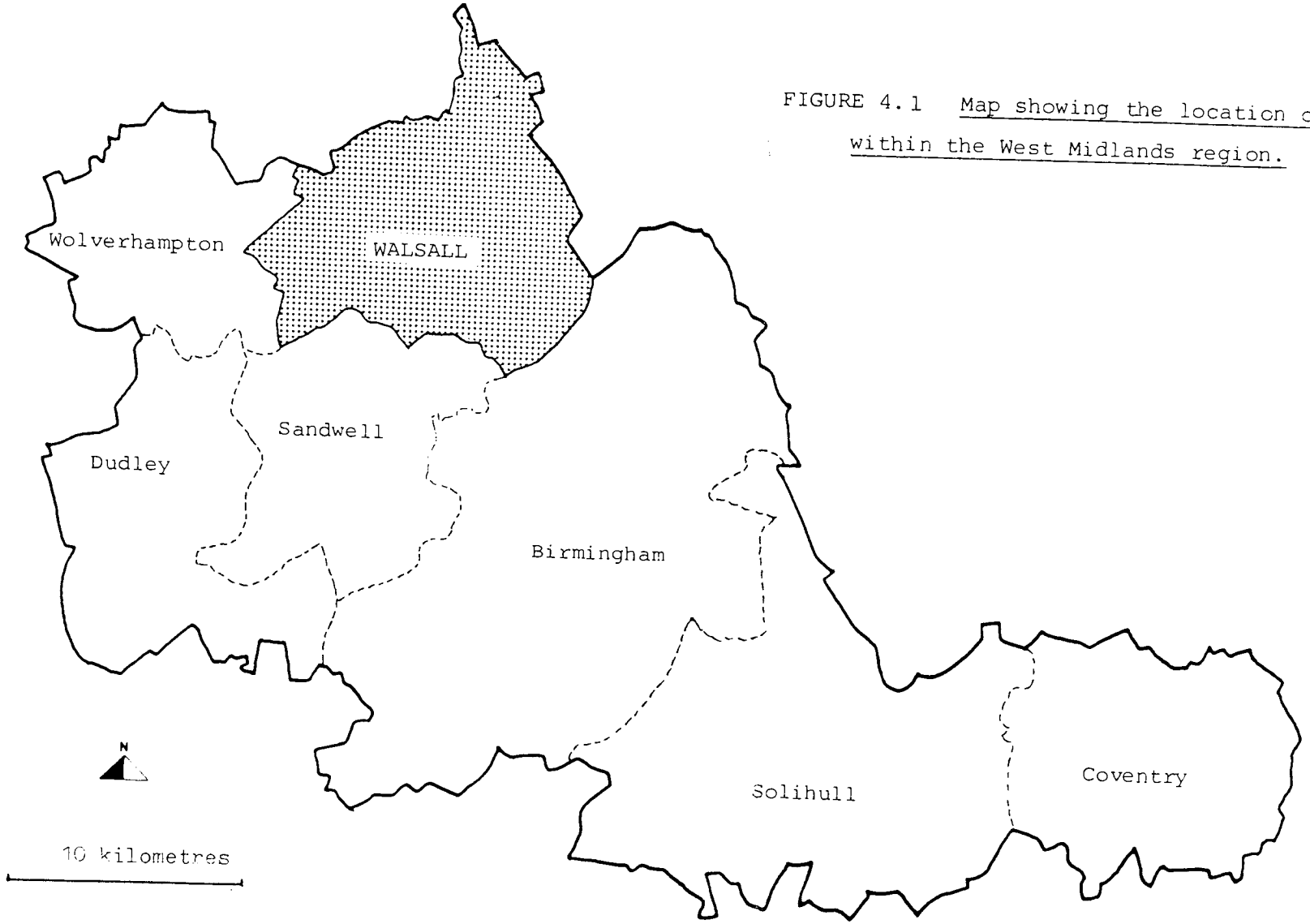


FIGURE 4.1 Map showing the location of Walsall within the West Midlands region.

The most appropriate experimental design for this research framework was taken to be that of a 'case-study' investigation of an urban area. Walsall Metropolitan Borough was selected for this case study. The location of Walsall is shown in Figure 4.1. Walsall was chosen as the case-study area for practical reasons already outlined in section 1.5; briefly these were:-

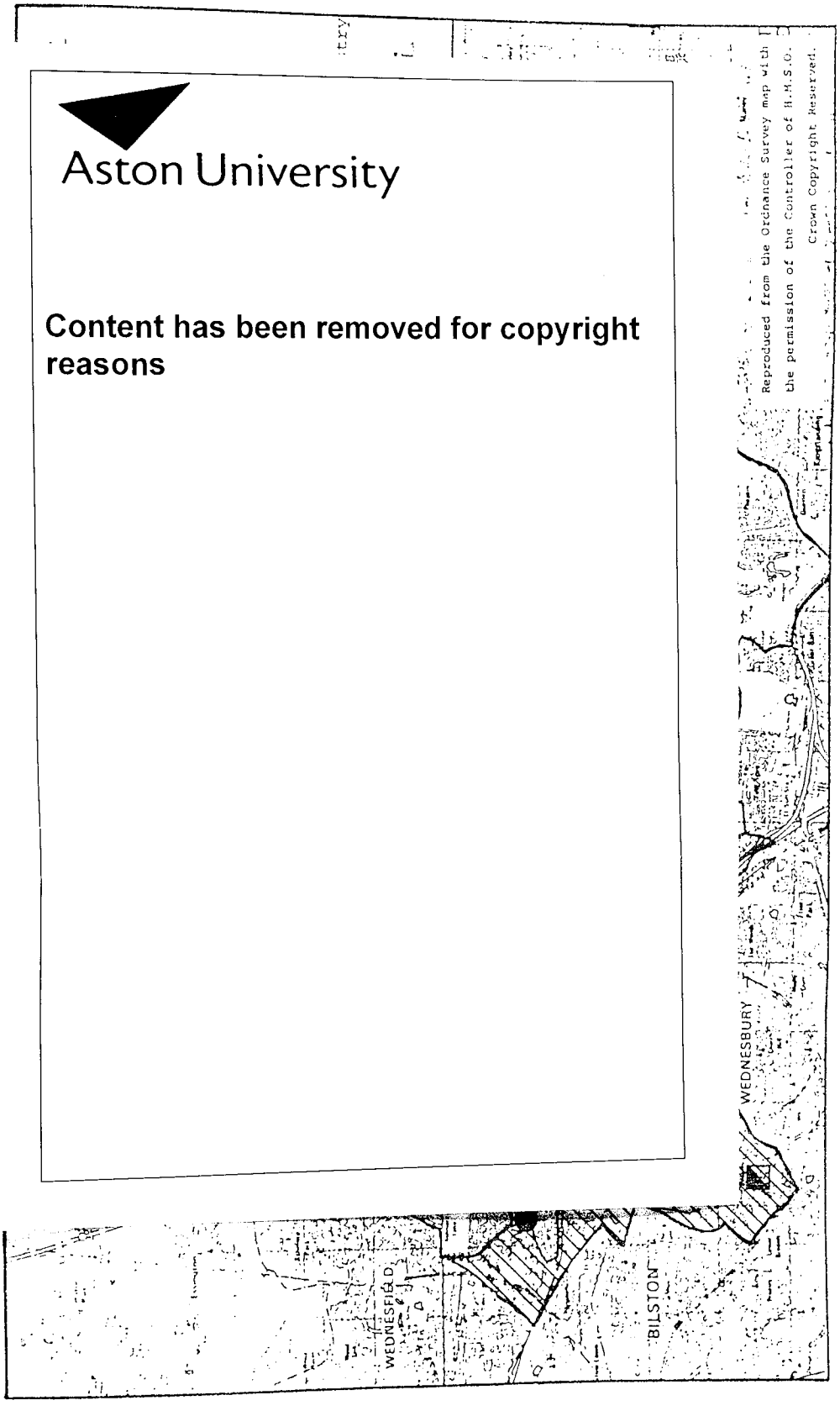
- previous research has demonstrated that the Walsall environment is contaminated by both lead and cadmium (eg Pattenden and Branson, 1982);

- there is a wide variety of land-uses in the Walsall area ranging from semi-agricultural to industrial;

- Walsall local authority were willing to co-operate with the study;

- there are a number of large metal based manufacturing plants in the borough which are likely to be sources of airborne metal emission. These include secondary copper refineries, ironfoundries and a zinc alloy works and numerous small plants which include plating works, galvanising works, lead casting, brass and bronze founding etc. The location of these major metal industries and more general metal industry areas is shown in Figure 4.2.

The remainder of this chapter details the practical and technical aspects of the research framework and the design of the experimental investigation of deposition in Walsall. The development of the theoretical aspects of the research framework are dealt with in the appropriate chapters later in the thesis (spatial variation in chapter 6 and source identification in chapter 7.)


Aston University
Content has been removed for copyright reasons
Reproduced from the Ordnance Survey map with
the permission of the Controller of H.M.S.O.
Crown Copyright Reserved.
WEDNESBURY
WEDNESFIELD
BILSTON

4.1.2 Structure of the chapter

Section 4.2 details the design, siting policy and analytical procedure involved in the use of the new deposition monitoring method which is referred to as the 'deposit cannister method'. Section 4.3 outlines the field survey sample frame design of the deposition monitoring surveys and section 4.4 gives the practical details relating to the execution of these surveys.

4.2 Design of the 'deposit cannister' deposition measurement method

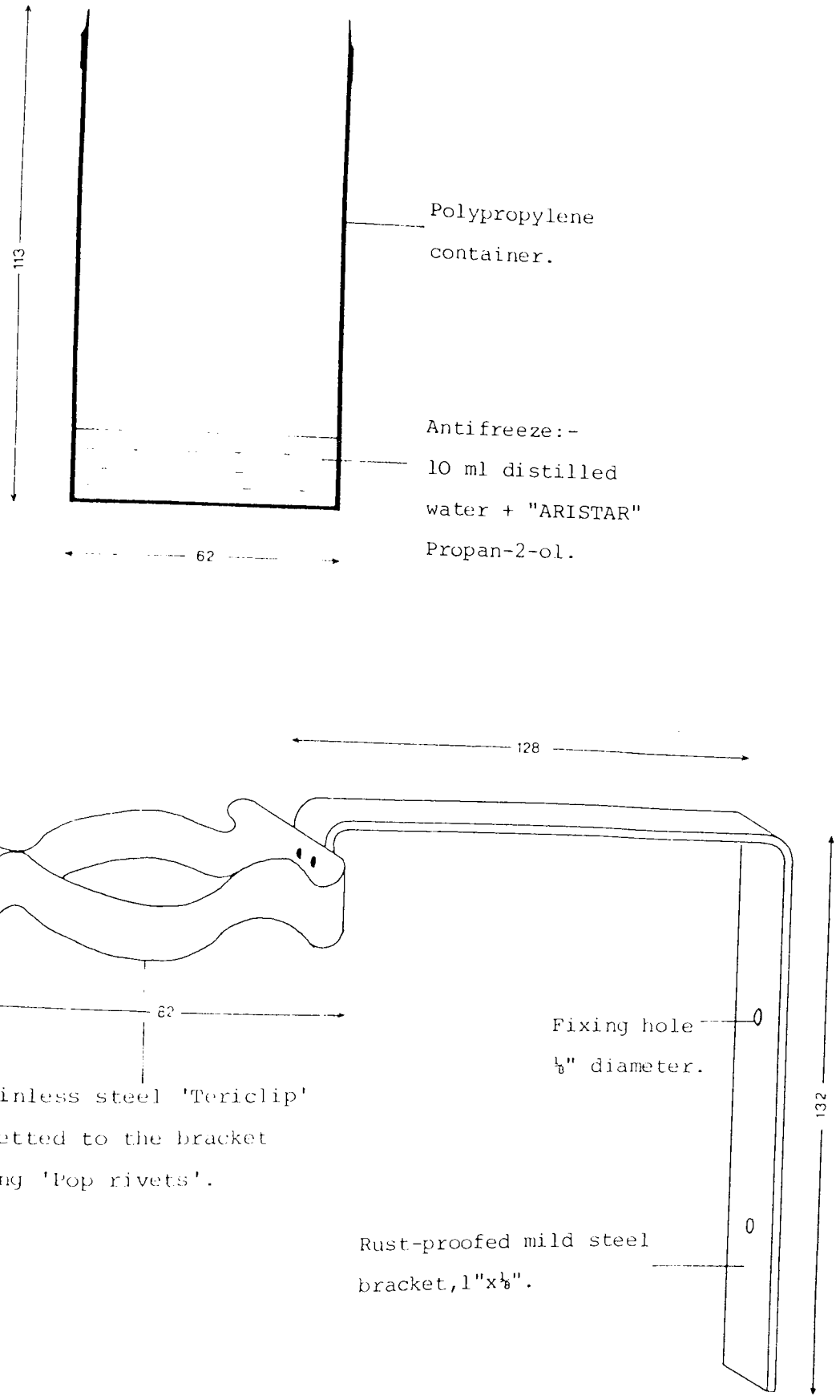
4.2.1 Background

The existing methods of quantifying deposition rates have been reviewed in section 2.3. The deposit gauge method has been identified as the most appropriate means of obtaining representative samples of vertical deposition (fallout and rainout). Of the standardised deposit gauges the I.S.O.G has been shown to be technically the most efficient sampling instrument. However, the review of these types of collection devices showed that they are bulky, expensive and necessitate the use of restrictive support frames. This means that there is little freedom in the siting of such instruments. This research has therefore taken the ISOG and simplified its design and supporting structure. This simplification has been achieved by reducing the size of the collection cannister. This allows more freedom in the siting of the instruments and greatly reduces the costs involved in purchase of equipment and operation of the technique.

4.2.2 Deposition measurement using the deposit cannister

The main criterion governing the degree to which the size of the collection container may be reduced is the availability of a container with the correct ratio of aperature to depth (ie one that equals the ratio of the ISOG) and which, over a four week collection exposure period, will still collect sufficient quantities of metals for these to be detectable using the analytical detection system (atomic absorption spectrophotometry). Warren Spring Laboratory have conducted wind-tunnel investigations using a 1/3 scale ISOG

FIGURE 4.3 The deposit cannister and fixing braket.



*note dimensions in millimetres.

(Ralph and Barrett, 1976). This represents $1/9^{th}$ of the collecting area of the full scale gauge and hence $1/9^{th}$ of the quantity of metal available for analysis. This was taken as an acceptable reduction. A suitable $\frac{1}{3}$ scale cannister was obtained from Johnsen and Jorgenssen Plastics Ltd of London. These were cheap, durable and of light construction (grey polypropylene). They were also supplied with 'clip-fit' lids which were used to seal the cannister following exposure. The containers were not found to contain heavy metal based pigments.

The deposit cannisters were small and light enough to be held in a simple clip bracket, even when full of water. The brackets were designed to be attached to convenient supports, mainly telegraph poles, using nails. The brackets were made from rust-proofed mild steel and chrome 'teri-clips' by Aston Services Ltd of Birmingham. The dimensions of the cannister and bracket are illustrated in Figure 4.3. Plate 4.1 shows the complete deposit cannister assembly. Plate 4.2 shows a deposit cannister in position on a telegraph pole at the height of six metres.

Telegraph poles were chosen as suitable supports because they are ubiquitous in the Walsall area and allowed a large number of cannisters to be sited. Of course telegraph poles located next to busy roads could potentially represent a source of bias to the survey due to resuspension of dusts through vehicle movement. For this reason poles next to busy roads were avoided in favour of more secluded sites in backstreets or open space, thus this potential problem was minimised.

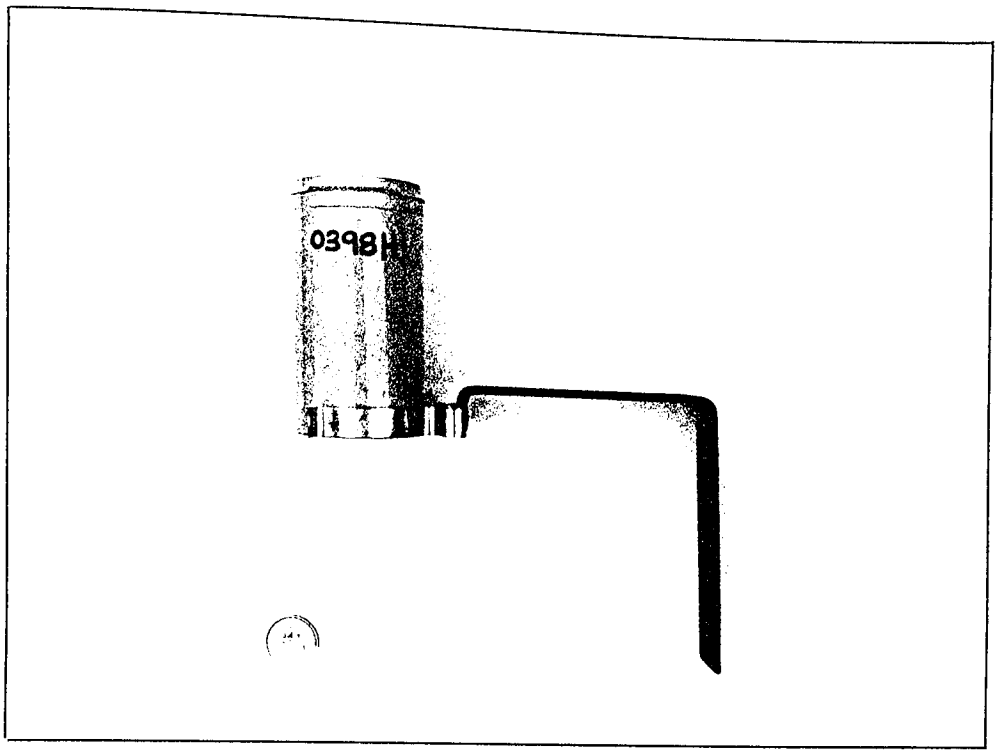


PLATE 4.1 THE DEPOSIT CANNISTER AND FIXING BRACKET.

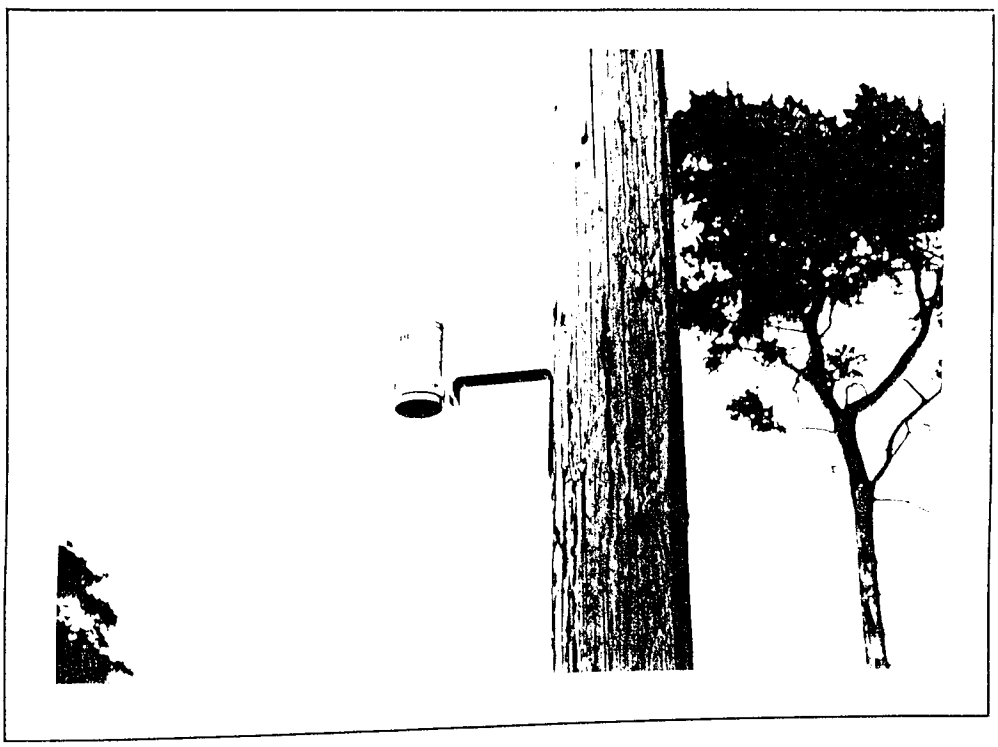


PLATE 4.2 DEPOSIT CANNISTER IN POSITION ON A TELEGRAPH POLE.

The sample height of six metres, substantially above that the ISOG of 1-2 metres), was selected in order to reduce the possibility of contamination from locally resuspended surface dust. This aspect of the measurement of deposition has not been investigated specifically in this research but represents an important area for future research.

As with any new experimental method, a series of investigations have been conducted to provided estimates of the 'errors of estimate' involved in the technique. The method of investigation to provide estimates of the precision of the deposit cannister method is described in section 4.3 and the investigations into sources of analytical error are detailed in Appendix B. The results are presented in chapter 5. A fieldwork comparison of the ISOG and the deposit cannister was attempted by parallel siting, however no results were obtained due to extensive gale damage. Therefore this important aspect of the investigation of measurement errors is an important priority for further research.

4.2.3 Laboratory analytical methods

The technical description of the analytical methods used to detect and quantify the metals in deposition samples is given in full in Appendix B. Briefly this consisted of volume reduction by evaporisation and wet ashing using hot concentrated nitric acid, followed by measurement by atomic absorption spectrophotometry. In addition to lead and cadmium, eight further metals were included in the analysis on the basis of their usefulness to the source tracing exercise described in detail in chapter 7, and also giving consideration to their detectability detected by atomic absorption.

These additional eight elements and the source types they were expected to be associated with were:

- aluminium: soil and coal combustion,
- arsenic: coal combustion,
- chromium: metallurgical industries,
- copper: copper refining,
- iron: iron and steel industry,
- magnesium: soil,
- mangenese: ironfounding,
- zinc: metallurgical industries.

The results of the experimental investigation into the performance of the deposit cannister and the results obtained from the investigation into analytical error are presented in chapter 5.

4.3 Field Survey Design

4.3.1 General outline of the field surveys

The field survey of deposition in the Walsall Metropolitan Borough case-study area was designed in four parts: the main survey and three supplementary surveys.

Survey 1: this was the main survey covering 243 sites in the Borough, and it was from these results that the major analytical source-identification exercise (Ob.3) and the general statistical distributions of deposition rates were determined.

Survey 2: this supplementary survey formed the basis for a detailed investigation of spatial variation in deposition rates at the sub-kilometre scale (Ob.2)

Survey 3: this was a 'hotspot' surveys carried out around a single major source using a snow-surface rather than the deposit cannister method (Ob.2)

Survey 4: this supplementary survey was designed to explore the sampling error of the deposit cannister method by conducting replicate sampling at several sample points (Ob.1).

The main features of these surveys and the functions they serve in relation to the research method as a whole are summarised in Table 4.1. The detailed survey designs are described in detail below.

Table 4.1 Summary of the main features of the four deposition surveys

Survey (No of sites)	Purpose	Spatial Structure
Survey 1 (243)	General levels, broader variability and input to source identification	27 Km^2 x 9 sites/ sq.km
Survey 2 (56)	Spatial variations at sub-kilometre scale.	2 Km^2 x 20 sites/ sq.Km 1 Km^2 x 16 sites/ sq.Km
Survey 3 (44) "Snow survey"	Hotspot investigation	44 sites on 4 transects of 1 Km length (11 sites per km. transect)
Survey 4 (18)	Measurement error	3 poles x 6 cannisters per pole

4.3.2 Survey 1 - sample framework

Survey 1 was designed to provide a large number of individual deposition measurements from a cross-section of land uses and industrial activities. The maximum number of measurements was limited to 250 by available resources. Practical siting difficulties restricted the number of measurements that could be made at each telegraph pole to a single cannister (restriction placed on survey by British Telecom for safety reasons). Therefore a maximum of 250 sites could be surveyed at any one time.

The survey was designed to provide a 'snapshot' of deposition which could be used to examine the broad-scale spatial differences in deposition error on urban area, as well as provide data for the modelling exercises.

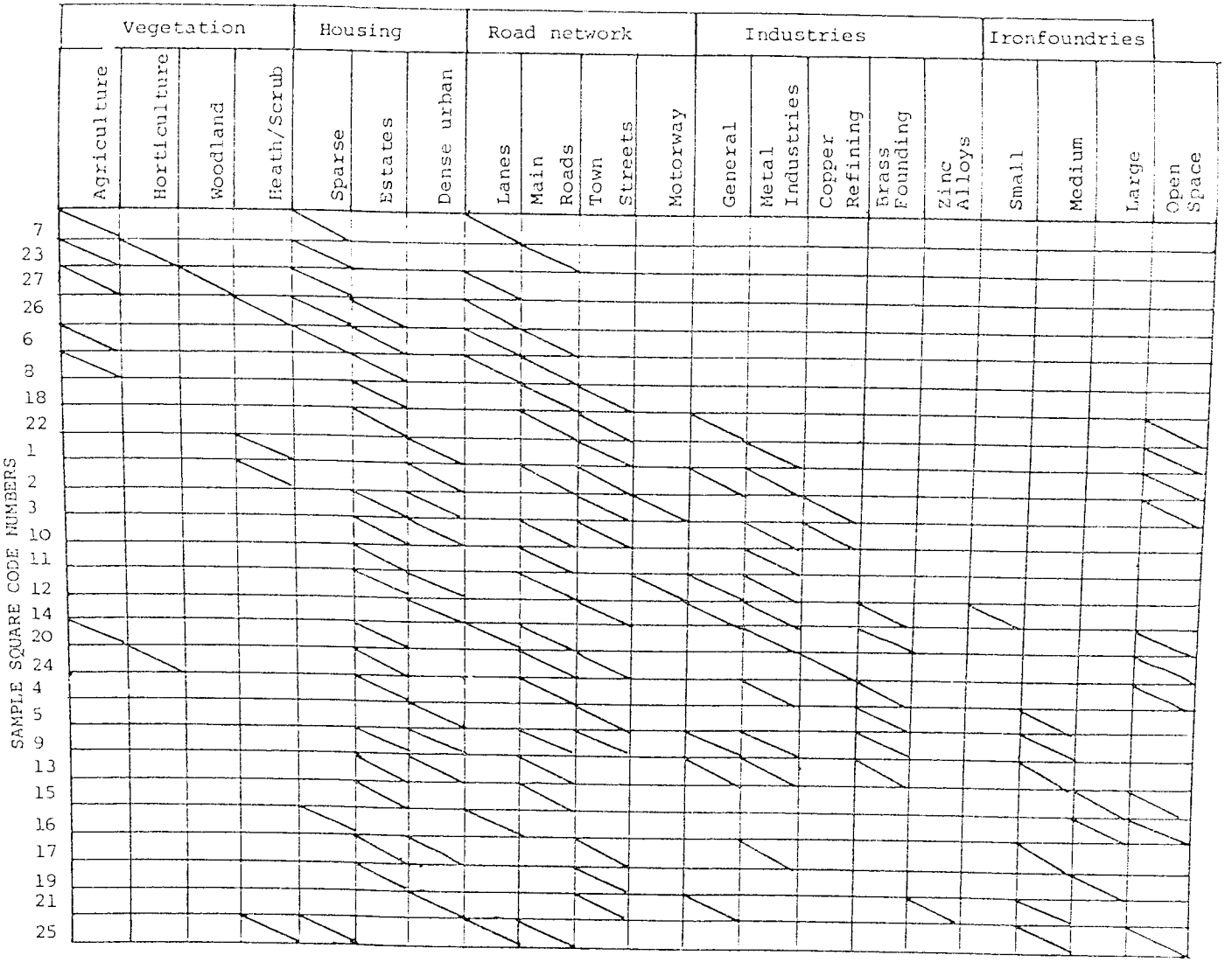


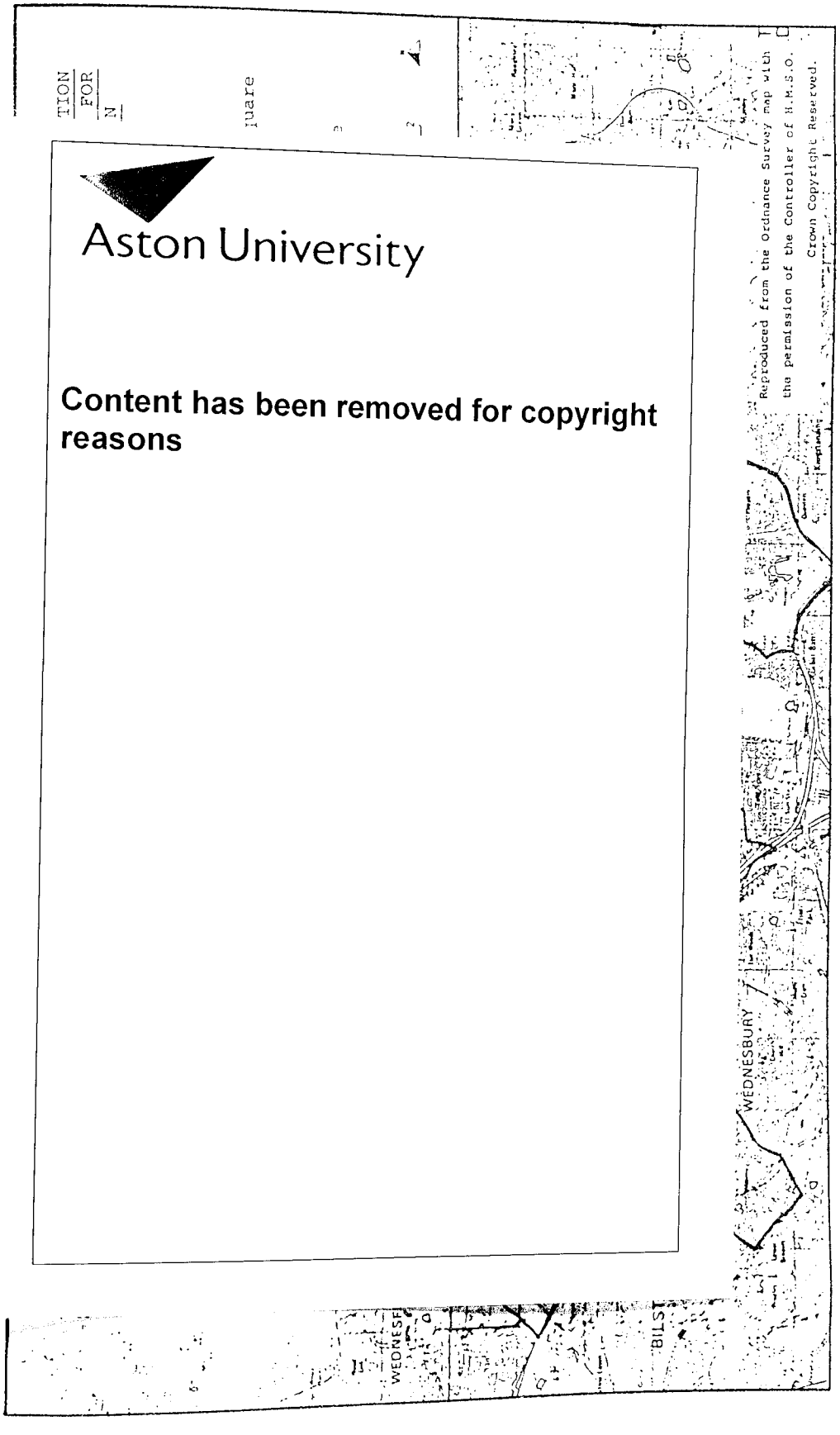
TABLE 4.2 LAND-USE ANALYSIS OF THE TWENTY-SEVEN SAMPLE SQAURES IN SURVEY 1.

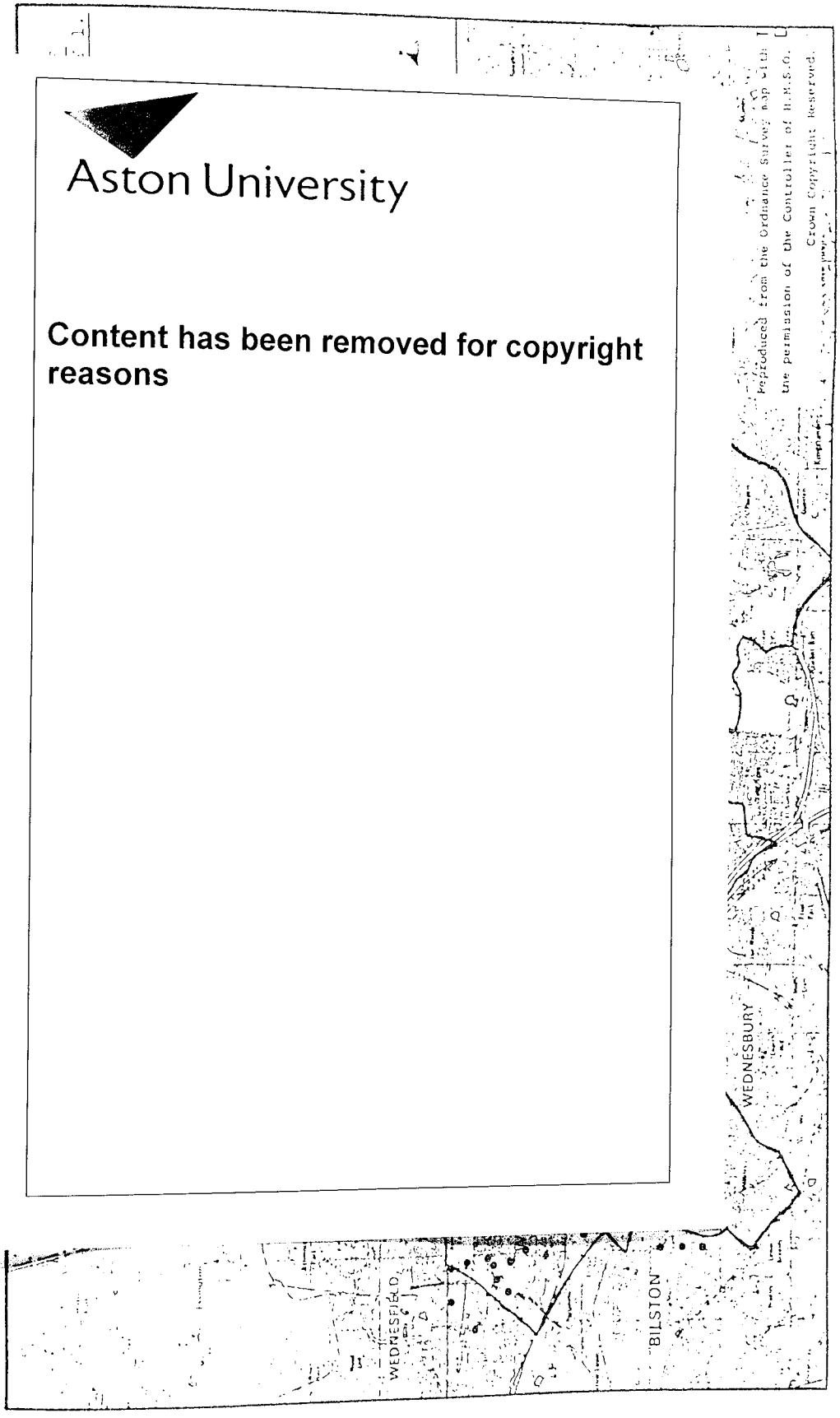
The sample framework was structured on 1.Km grid-square area unit sampled from the 1 kilometre Ordanance Survey grid. The sample density within sample squares was restricted by the availability of suitable sample sites and this was judged to be a maximum of nine sites per grid square. However, it was recognised that ideally sample density should be determined by the within-square variance of deposition and the number of independent measurements required to obtain a given standard error of estimate of a grid square mean (Som, 1973). The within-square variance of deposition levels was not known prior to the research; indeed it was an objective of the research to provide this basic information which might than be so applied to future surveys.

With a practical limit of 250 deposit cannisters and a sample density of 9 sites per 1 kilometre square, the maximum number of Km squares that could be sampled was 27. These were selected on a structured basis to provided a cross-section of all land-uses in the Walsall area. Table 4.2 gives a breakdown of the area land-uses and industrial activities contained within each sample square. The location of the 27 squares is given in Figure 4.4 and the location of each individual sample site is shown in Figure 4.5. Sample sites were selected on a structured-random basis using a 3x3 lattice, sites being taken as near as possible to the nodes of the lattice.

4.3.3 Survey 2 - sample framework

The second deposition survey was designed to provide estimates of the spatial variability of deposition rate at different sub-kilometre scales within a range of land-use types. This spatial


Aston University
Content has been removed for copyright reasons
Reproduced from the Ordnance Survey map with
the permission of the Controller of H.M.S.O.
Crown Copyright Reserved.
WEDNESBURY


Aston University
Content has been removed for copyright reasons
WEDNESBURY
BILSTON
WEDNESFIELD
Reproduced from the Ordnance Survey map with
the permission of the Controller of H.M.S.O.
Crown Copyright Reserved.

analysis was conducted at two levels; i) the location defined as 100 metres^2; and ii) the area defined as 1 kilometre^2. As already mentioned, spatial differences at a third level, greater than 1km^2 (the urban scale) were examined in survey 1. 'Location' variations were estimated by siting clusters of four cannisters within areas selected to cover a range of environments. 'Area' variations were examined by siting five separate clusters within a 1Km^2 area and by using the within-square variance obtained from the 'Survey 1' results. Broad scale 'urban' differences were examined using the differences between the 27 grid square means obtained from survey 1. Details of the location of these sample sites for survey 2 are given in the discussion of the results in section 6.3.2.

4.3.4 Survey 3: Hotspot survey

The investigation of the finer-scale spatial variations of deposition around an industrial source was conducted using the snow-surface technique. Forty-four samples were taken downwind of a secondary copper refinery on four cross-wind transects running N-S, on an occasion in 1982 when heavy snow had fallen and lain undisturbed for 5 days The details of the design of this survey are given in Appendix C.

4.3.5 Survey 4: investigation of measurement error

This investigation was conducted to provide the necessary estimates of precision for the deposit cannister method, expressed in terms of a measurement error. Six replicate cannisters were sited on single poles in three locations. Differences in the results

obtained from the cannisters at a single pole can be used for estimate the measurement errors arising from the combined effect of analytical errors, and instrument errors which include sheltering by the pole, microspatial and random variations in deposition (deposition of very large but infrequent particles is essentially a random process), variations in the size of cannister aperture and vertical positioning, splash etc (see Figure 2.4)

4.4 Execution of field surveys: practical details

4.4.1 Siting procedure

This section details the procedures used during the execution of the deposition monitoring exercises. The practical details concerning the snow survey (Survey 3) are given in Appendix C.

The deposit cannisters were acid rinsed, dried and sealed with clipfit lids and stored in the laboratory until use. On site, a suitable telegraph pole was identified according to the sampling framework described in section 4.3 and taking into account the following site selection criteria:

- height of 6 metres $\pm$ 1 metre.
- no immediate obstructions to wind field,
  buildings must subtend 30° horizontal elevation.
- site should be representative of surrounding areas and
  not unduly influenced by unrepresentative sources (eg busy
  roadside sites)
- vertical exposure should be unrestricted by overhead cables etc.
- easy access.

Using a collapsible ladder the bracket was positioned and nailed to the pole at the required height. The cannister was unsealed and labelled with a reference number. Anti-freeze was added (10ml of ARISTAR Propan-1- ol in distilled water) to prevent freezing and possible splitting of the cannister. The cannister was then attached to the bracket.

The cannisters were collected approximately thirty days later by the reverse procedure. Samples were transported back to the laboratory where they were acidified with nitric acid (ARISTAR grade) and stored in a refrigerator until they were analysed using the procedure described in Appendix B.

4.4.2 Survey 1

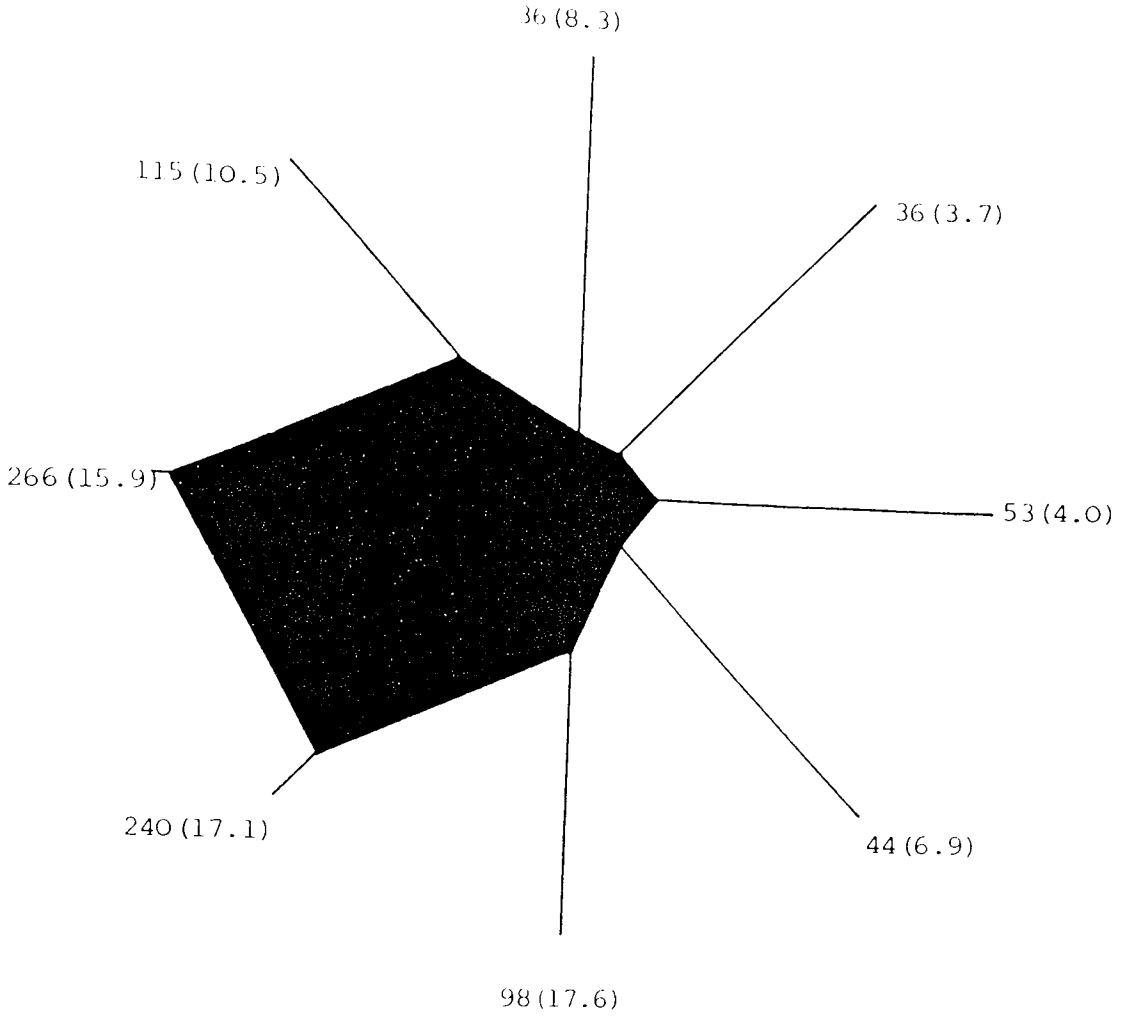
This survey was conducted during the period 15 November to 21 December 1982. On average it took two hours to position the nine cannisters in each sample square and two weeks to install and then collect all 243 cannisters in 27 samples squares. The recovery rate was 90.1% (cannisters were lost due to wind damage, vandalism, and/or spillage). The minimum number of cannisters recovered from any square was five and the average recovery was eight.

4.4.3 Survey 2

Survey 2 was conducted during the period 10 February to 10 March 1983 when sufficient cannisters were available. The recovery rate was slightly lower at 85.9% with the largest losses being at a residential square where five out of six gauges at a single site (a survey 4 site) were lost. The samples were analysed at the same time as the survey 1 samples.

4.4.4 Survey 4

Survey 4 was conducted at the same time as survey 2. Six replicate cannisters were placed at each of three sites. Only two of these sites returned sufficient measurements to allow statistical analysis.



Total number of hours = 888

Mean windspeed = 13.8 mph

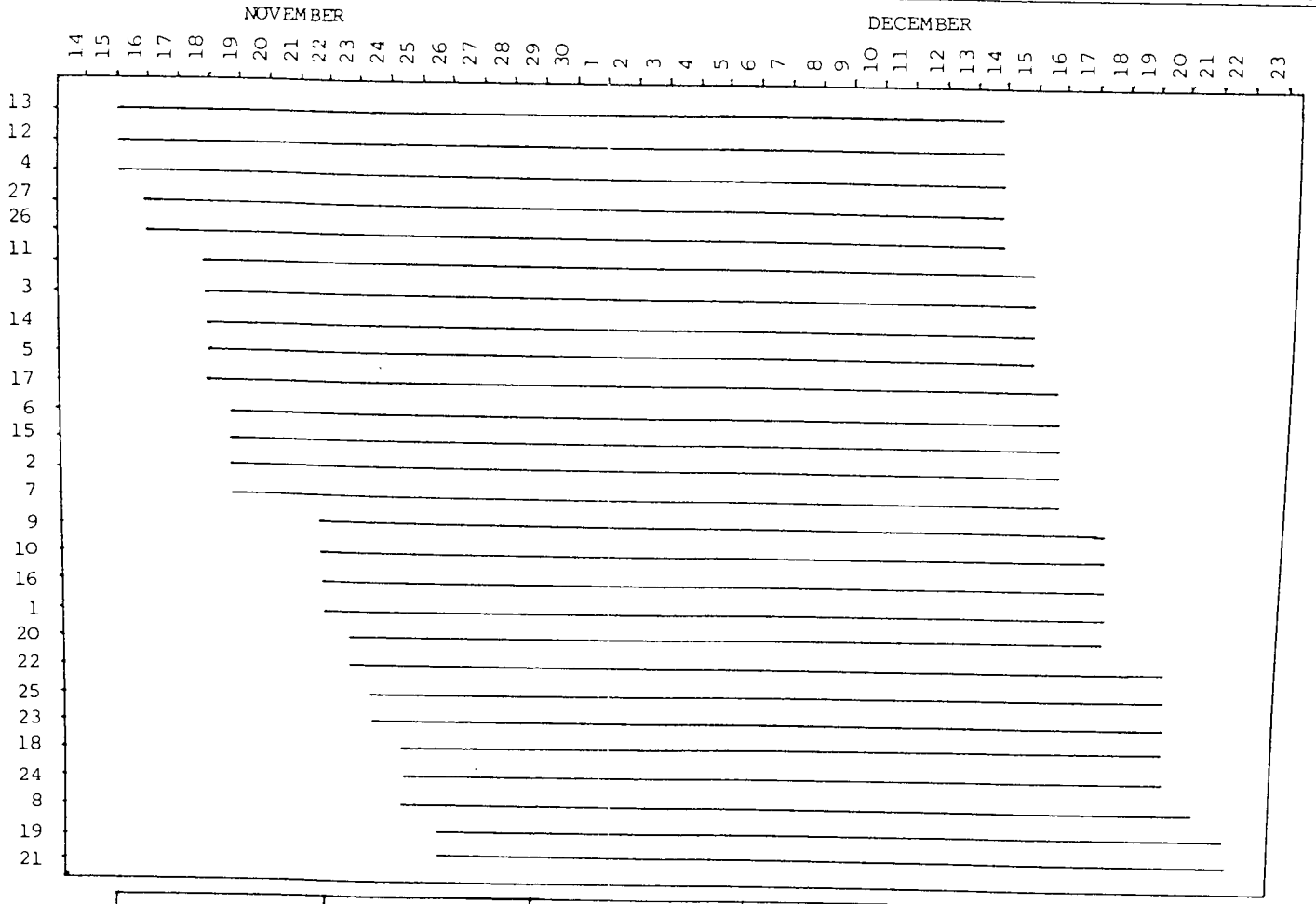
FIGURE 4.6 Wind direction and speed for the main sample survey during Nov-Dec 1982. Figure in parentheses is mean directional velocity, figure outside parentheses is directional frequency in hours.

(the urban square returned 4 cannisters and the rural square returned 6 cannisters).

4.4.5 Exposure conditions during the main survey

Deposition is a process strongly influenced by meteorological conditions, e.g high windspeed reduces deposition by sedimentation etc. The wind rose for the main sample period, Nov-Dec 1982, is given in Figure 4.6. This demonstrates that winds were largely from the S-NW directions and that mean windspeeds were highest when the wind was in the S and lowest to the NE. Rainfall of 97.0 mm was recorded during the six weeks period. Table 4.3 shows how the meteorological conditions varied for each grid square during its exposure and the degree of overlap between the exposure periods. It is inevitable that these differences in meteorological conditions will have resulted in discrepancies in the data set; however, they were not felt to be sufficient to warrant specific investigation, because for the greater part of the survey period all sites were exposed simultaneously.

TABLE 4.3 The exposure periods for the twenty-seven sample squares and a summary of weather conditions.



Mean windspeed- General direction	19.8 mph	14.0 mph	6.1 mph	10.6 mph	16.4 mph
	N,NW,SW	SW,S,W	NW,E,SE,S	NE,SE,SW,S W	NW,W,SW

4.5 Conclusions

This chapter has established the research framework and the experimental design that has been used to investigate the research problem of heavy metal deposition in urban areas. Chapter 5 now goes on to discuss the results of the deposition surveys and the findings of the investigations into measurement and analytical errors associated with the deposit cannister deposition measurement method. The exploration of spatial variation of heavy metal deposition levels is reported in Chapter 6 and the development of the source and receptor models to explain the sources of heavy metals is considered in chapter 7.

CHAPTER 5

5. ANALYSIS OF RESULTS: MEASUREMENT ERROR OF THE DEPOSIT CANNISTER

5.1 Introduction to the error analysis method

5.1.1 Outline

This chapter examines the experimental investigations that have been used to explore the performance of the deposit cannister deposition measurement method (Ob.1). These investigations consist of two component 'experiments'. The first was designed to estimate the error of the entire deposition measurement technique (measurement error). The second was designed to quantify the proportion of the measurement error attributable to laboratory analysis (analytical error). The remaining proportion of the measurement error was denoted as 'instrument error'.

5.1.2 Performance Evaluations of the Deposit Cannister Method

The adequacy of performance of a scientific measurement process can be judged using four general criteria:

i) the relevance of the measurement method to the demands of the scientific context;

ii) the extent to which it is repeateable;

iii) the reliability and representativeness of the results;

iv) the practical constraints associated with its use.

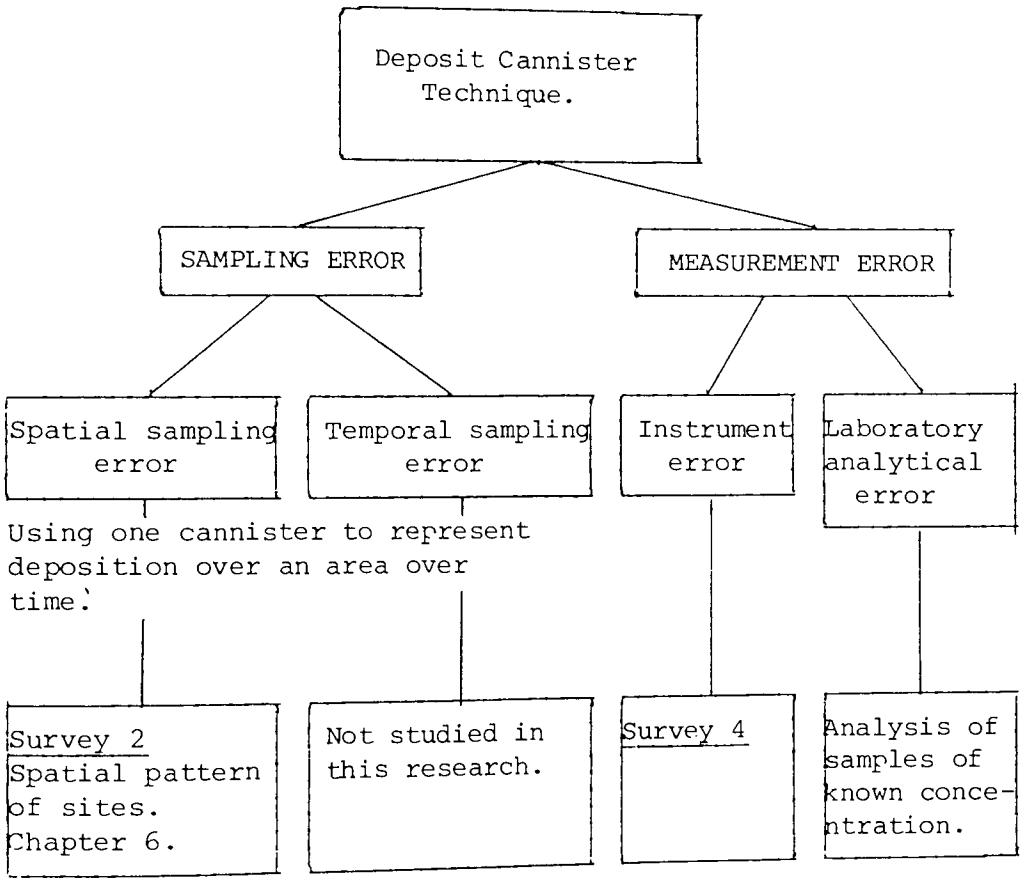
The deposit cannister measurement instrument and the associated

siting and analytical procedures have been specifically designed to meet the first, second and last criteria (discussed in chapters 3 and 4). This chapter is concerned with the general issue of the reliability and representativeness of measurements, which will be governed by two key elements of error: measurement error and sampling error.

Measurement error consists of two components: instrument error (i.e errors equivalent to those previously discussed in section 2.3 which are outlined in Figure 2.4) and laboratory analytical error. These govern the reliability of measurements made using the deposit cannister technique and hence the degree to which the technique satisfies the second criterion given above. This aspect of the evaluation of the deposit cannister is dealt with in detail in this chapter. Sampling errors are those errors that arise in using a single measurement to represent a variant entity. In the case of deposition, it is established that deposition rates vary over space and over time. The deposit cannister is a measurement method that records the deposition rate at one spot over a 30 day period. When the result is interpreted as representing the average conditions existing at a site or over a wider area and over a longer period of time, there will be an 'error of estimate' in using sample data to represent the average. This sampling error will consist of two sub-components: spatial sampling error, and temporal sampling error. Temporal sampling error has not been addressed in this research and so will not be discussed further. Spatial sampling error has been investigated (in particular through Survey 2) and the results are reported and discussed in chapter 6.

The general structure of the research method used in pursuing the

TABLE 5.1 Structure of the measurement error and the sampling error of the deposit cannister technique and an outline of the various experiments that have been conducted to investigate the component errors.



error analysis is summarised in Table 5.1.

5.1.3 Investigation of measurement error

Measurement error affects all measurement systems and can arise either from random variations or from systematic variations which may be inherent in the measurement process. Random variations, typically referred to as 'noise' affect the overall precision of measurements. Systematic variations, often referred to as 'bias', influence measurement 'accuracy' and cause measurements to over-or under-estimate the 'true' level of the entity being measured (Eckshlager 1969). One way in which random and systematic error can be quantified is by replicating measurements of samples whose exact composition is known. In this way the random error can be expressed in terms of an error variance,[1] and the systematic error can be expressed as a bias which is the difference between the observed c and the true concentration level of the substance C by $C-c$. This research has used the technique of replication to provide estimates of instrument error and analytical error. The various experiments that have been used for this purpose are outlined in Table 5.1.

---

1. Error variance , σ^2 of n replicate observations, x_1, x_2, x_3 ...., xn is given by:

$$\sigma^2 = \frac{\sum_{i=1}^{N} (x_1 - \bar{x})^2}{N - 1}$$

and can also be expressed as the standard deviation, σ which is the square root of the variance. (Chatfield, 1978)

The research had originally aimed to estimate the bias of the deposit cannister by experimental comparison with the ISOG. However, no results were obtained from the fieldwork investigation because the experiment was destroyed by gale damage. Therefore this important aspect of the evaluation of the deposit cannister remains to be completed and is a high priority for further research.

5.1.4 Chapter structure

Section 5.2 examines the results of the experimental investigation (Survey 4) using 6 replicate cannisters at a single site and derives estimates of the measurement error of the deposit cannister method in terms of an error variance σ^2_m. Section 5.3 then examines the errors involved in the laboratory analysis of deposition samples and derives estimates of analytical error, σ^2_c and bias, $C - \bar{c}$. This section then goes on to examine the various stages of the analytical process in more detail and derives estimates of the errors associated with each stage. Section 5.4 contains the main conclusions of the chapter and also details how an estimate of the instrument error of the deposit cannister has been obtained using the principle of addition of variances.

5.2 Measurement Error, σ_m^2

5.2.1 Standard errors of estimate for a single deposit cannister

This section describes the results of the investigation into the repeatability of deposition measurements and considers how this may affect the design of deposition monitoring exercises.

The experimental procedure (Survey 4) for quantifying the error of estimate of using a single cannister to quantify deposition at a site has been outlined in section 4.3. Briefly this consisted of siting 6 replicate cannisters on a single telegraph pole at each of three sites taken to represent of different types of environment; rural, residential and urban. Only the rural and urban data are available for analysis (the residential site was vandalised). This gives two independent estimates of σ_m. These are given in Table 5.2. From these results the site mean lead deposition level is shown to be significantly greater at the urban site compared to the rural site (tested using students t-test at 99% probability level[1]). The difference in cadmium deposition between the two sites is not significant. The variances of deposition levels at each site are not statistically significantly different when compared using the F- ratio test (F = S 1/ S 2) and can therefore be taken as independent estimates of the single population variance, σ_m^2

---

1 The t-test is used to statistically compare two sample means $\bar{X}_1$ and $\bar{X}_2$ and is of the general form:-

$$t = \bar{X}_1 - \bar{X}_2 / S\sqrt{(1/n_1 + 1/n_2)}$$

where the combined estimate of variance is given by

$$S2 = \frac{(n - 1)\, S1^2 + (n - 1)\, S2^2}{n_1 + n_2 - 2}$$

(Chatfield, 1978)

Table 5.2 Results of siting six replicate deposit cannisters at one site ($mg/m^2/30$ d).

Lead

Cannister	Urban area n=4	Rural area n=6	F	t
1	0.95	0.21		
2	1.11	-		
3	0.76	0.05		
4	1.07	0.09		
5	-	0.04		
6	-	0.02		
Mean	0.973	0.082		**
Standard deviation	0.157	0.076	-	

Cadmium

Cannister	Urban area n=4	Rural area n=6	F	t
1	0.03	0.04		
2	0.04	-		
3	0.04	0.03		
4	0.01	0.01		
5	-	0.05		
6	-	0.04		
Mean	0.030	0.034		-
Standard deviation	0.014	0.015	-	

(* $p \leq 0.05$ ** $p \leq 0.01$)

(Yeomans, 1968). Thus, measurement error appears to be independent of the environment the measurement was taken in and therefore it is justifiable to used a pooled variance estimate of σ^2_m. This

pooled estimate is given by averaging the variances;-

Lead

$$= (\sigma^2_{rural} + \sigma^2_{urban})/2$$

$$= \sqrt{(0.076^2 + 0.157^2)/2}$$

$$\sigma_m = \underline{0.123 \text{ mg/m}^2/30 \text{ days}}$$

and Cadmium

$$= \sqrt{(0.015^2 + 0.014^2)/2}$$

$$\sigma_m = \underline{0.015 \text{ mg/m}^2/30 \text{ days}}.$$

Measurement errors for the remaining elements have been calculated in a similar fashion and are given in Table 5.3.

5.2.2 Implications of σ^2_m for the design of deposition measurment surveys

The precision with which deposition can be measured will influence the number of independent measurements that are required to estimate site deposition rates to within given levels of confidence. For example, if the measurement error in relation to site mean deposition levels is excessive then a very large number of independant measurements must be taken to estimate site mean deposition levels reliably. For practical reasons this research has used a sample density of one cannister per site in order to allow a large number of sites to be surveyed. However, if the aim of the study had been to examine the level of deposition occurring at certain specific sites (for example in order to assess whether deposition at a particular site exceeded a given level), then consideration of the sample number would have been more crucial. The number of separate

Table 5.3 Standard error of estimate of a site deposition level using a single deposit cannister for metals other than lead and cadmium

	Measurement error σ_m ($mg/m^2/30d$)
Aluminium	1.75
Arsenic	0.004
Chromium	0.04
Copper	0.16
Iron	2.39
Magnesium	0.92
Manganese	0.09
Zinc	6.64

deposition measurements required to obtain a given error of estimate for a site mean deposition level can be calculated using the values of measurement error obtained in the proceeding paragraphs. If the assumption is made that this measurement error follows a Normal distribution (distribution approximates to a Gaussian Normal Distribution), then using the estimates of the population measurement error Om, the confidence intervals for measuring a true site deposition rate $\bar{x}$, are given by:-

$$\text{probability } (\bar{x} - 1.96\frac{\sigma_m}{\sqrt{n}} < \mu < \bar{x} + 1.96\frac{\sigma_m}{\sqrt{n}}) = 0.95$$

(Caulcott and Boddy, 1983)

This gives the 95% confidence interval for the true site mean deposition rate. The 99% confidence interval for the site mean lies within 2.58 standard deviations of the sample mean. Thus, the

99% confidence interval is given by:

$$\bar{x} \pm 2.58 \frac{\sigma_m}{\sqrt{n}}$$

The 68% confidence interval lies within 1.0 standard deviations from the mean and is given by:-

$$\bar{x} \pm \frac{\sigma_m}{\sqrt{n}}$$

Table 5.4 contains estimates of the confidence intervals for true site deposition levels for a range of possible replicate samples, n.

Table 5.4 The Confidence intervals at different probabilities for estimating site deposition rates using between 1-20 replicate cannisters per site.

Confidence interval ($\pm$ mg/m^2/30d).

Sample number, n	$\frac{\sigma_m}{\sqrt{n}}$ = 68%	1.96 $\frac{\sigma_m}{\sqrt{n}}$ = 95%	2.58 $\frac{\sigma_m}{\sqrt{n}}$ = 99%
Lead			
1	0.123	0.241	0.317
2	0.087	0.170	0.224
3	0.071	0.139	0.183
4	0.062	0.121	0.159
5	0.055	0.108	0.142
10	0.039	0.076	0.100
15	0.032	0.062	0.082
20	0.028	0.054	0.071
Cadmium			
1	0.015	0.029	0.039
2	0.011	0.021	0.027
3	0.009	0.017	0.022
4	0.008	0.015	0.019
5	0.007	0.013	0.017
10	0.005	0.009	0.012
15	0.004	0.008	0.010
20	0.003	0.007	0.010

5.2.3 Comparison between the measurement error of the deposit cannister and the ISO deposit gauge

The ISO deposit gauge represents the standardised version of the deposit cannister. As yet there has been no detailed investigation of the precision of the ISO method (Cunningham, 1984). Crossley and Hill (1982) however, have conducted a limited investigation of the precision of the standardised gauge by exposing two identical ISO gauges simultaneously at a single site and making monthly lead deposition measurements over a period of 2 years. These results can be used to obtain estimates of measurement error. Using Crossley and Hills original results the measurement error, σm of a single lead deposition measurement can be derived from the monthly differences, d, between the individual gauge measurements $X_1 j$ and $X_2 j$. If the observed average difference is denoted by $\bar{d}$ and the standard deviation of the observed differences by Sd, then the standard error of d is given by $Sd/\sqrt{K}$ and the standard error of the single deposition measurements, σr is given by $Sd/(\sqrt{K} \cdot \sqrt{2})$. This gives the standard error of a single lead deposition measurement σm of 0.282 $mg/m^2/30$ days. This compares to σm for the deposit cannister of 0.123 $mg/m^2/30$ days. Clearly and surprisingly the measurement error of the deposit cannister is less than that of the ISO method used by Crossley and Hill (1982). However this comparison is affected by four potential sources of variance which have not been taken into account and which make direct comparsion difficult:

- the ISO gauge estimate of σm is based on all-year-round measurements, while the estimate of σm for the deposit cannister is based on a single month's measurements;

- there are differences in the analytical methods employed in the two studies;

- the mean lead deposition rate in the Crossley and Hill study was over four times greater than that observed during this present ambient investigation (σ_m may increase over this range of deposition rates).

- there is reasonable evidence of a constant systematic bias between the two gauges employed by Crossley and Hill (estimates of site mean obtained from their ISOG 2 are significantly lower than the estimate of ISOG 1 as tested by a t-test at 95% confidence level[1]).

Clearly further research is necessary in order to allow these differences in measurement precision to be investigated and it is not possible at this stage to say whether the apparent increase in measurement precision for the deposit cannister represents a real improvement. However at a general level it appears that the deposit cannister is likely to be at least as effective as the standard ISO deposit gauge.

1. t-test of the form

$$to = \frac{\bar{d}}{Sd/\sqrt{K}} = 2.25 \ *$$

* (t 5% with 20 degrees of freedom = 2.086)

5.3 Laboratory analytical error, σ_c

5.3.1 Introduction

This section examines the results of the experimental investigation of laboratory analytical errors. This section is divided broadly into two parts. The first part (5.3.2) deals with the investigation into analytical error of the entire analytical method using the results of replicate analyses of artifical deposition samples of known concentration. The second part of the chapter (5.3.3) examines in disaggregate the errors arising at various key stages in the analytical process (ie evaporation, digestion, dilution and determination). This investigation consists of analyses of 'blank' samples (ie samples whose concentration is zero) in order to detect sources of positive bias (contamination).

5.3.2 Results of the investigation into laboratory analytical error

Analytical error has been investigated using artifical 'deposition samples' whose exact concentration was known. These samples were made up using analytical standard solutions added to empty deposit cannisters and then analysed in the normal fashion (described in Appendix B). Two series of experiments were conducted. In the first six replicate analyses of a standard concentration C, of 1.0 ug/ml was used for all ten metals to provide estimates of σ_m^2 and $C-\bar{c}$ for each metal. In the second experiment a range of C concentrations were analysed in order to investigate whether error is independant of concentration or whether it is a function of the concentration.

Table 5.5 Results of the analysis of 6 replicate samples of known concentration C of 1.0 ug/ml

	ug/ml $\bar{C}$	σ_c	te_1
Pb	0.62	0.11	**
Cd	0.73	0.02	**
Al	0.47	0.16	**
As	0.85	0.02	**
Cr	1.17	0.24	
Cu	0.93	0.04	**
Fe	1.04	0.05	
Mg	0.93	0.05	*
Mn	-	-	
Zn	1.35	0.43	

* te 5% = 2.015 ** te 1% = 3.365

a) analysis of samples for which C = 1.0 ug/ml

Table 5.5 contains the results of six replicate analyses of samples where C equals 1.0 ug/ml. From these results it is clear that for both lead and cadmium the mean recovery, $\bar{c}$ is less than 100%. For lead the recovery rate is 62% and for cadmium it is 73%. In both cases this loss is statistically significant as shown by the results of the t-test. Metal loss could be explained by precipitation, glass adsorption, volatilization or detection errors (e.g calibration/set-up errors, interference etc). These types of error are discussed in detail in many standard texts (e.g. Minezewski, 1982).

1 The t-test was of the form

$$t = \frac{(C - \bar{c})n}{\sigma_c}$$

(Chatfield, 1978)

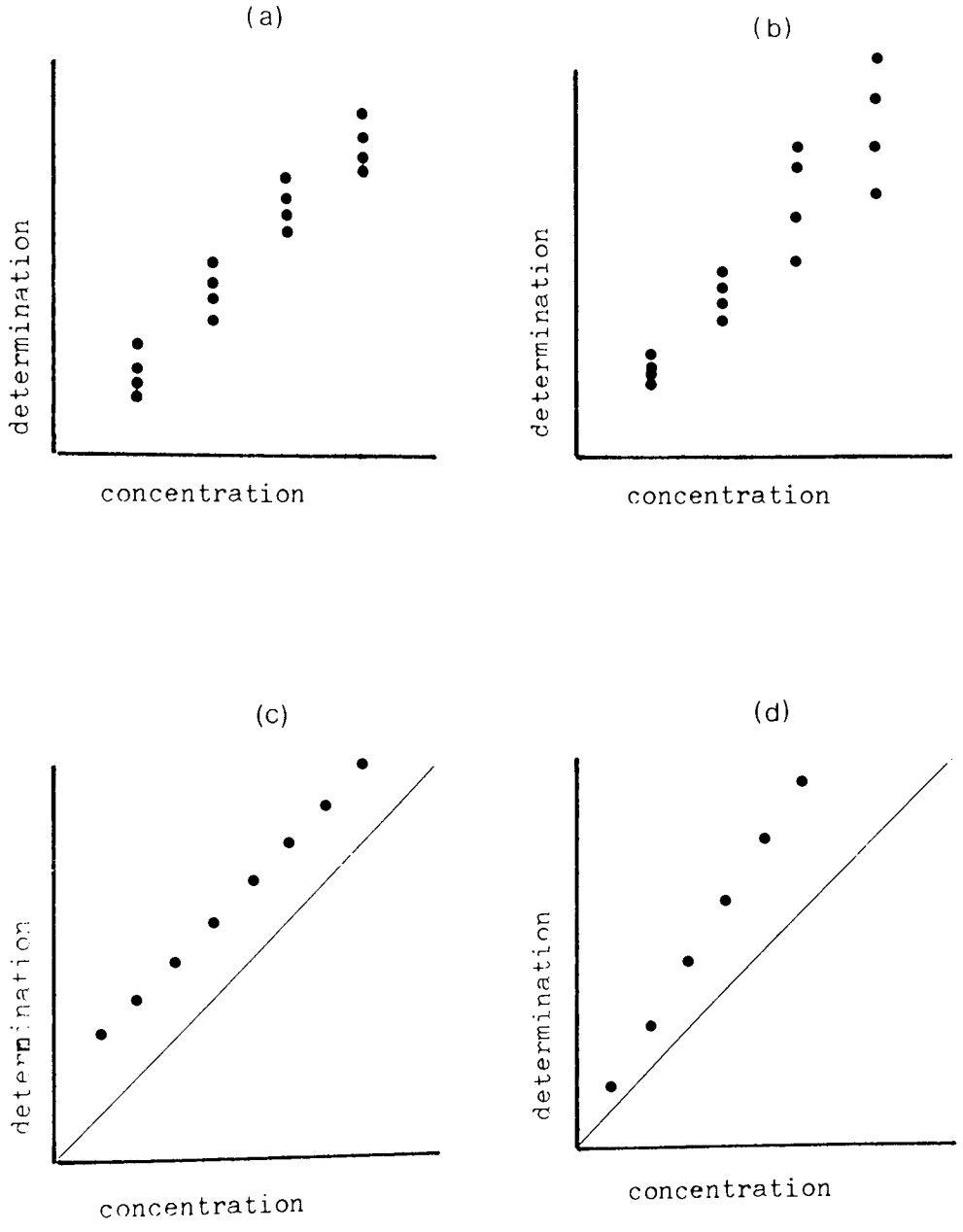


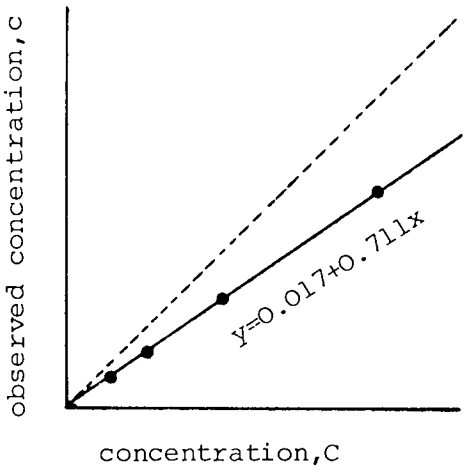
FIGURE 5.1 DETERMINATION ERRORS AND CONCENTRATION, a) evidence of constant precision, b) evidence of decreasing precision with increasing concentration, c) evidence of fixed bias, d) evidence of relative bias.

The random analytical error, given in Table 5.5 as a standard deviation σ_c, is proportionately more important for lead than for cadmium (ie the coefficient of variation for lead is 18% as compared to only 3% for cadmium).

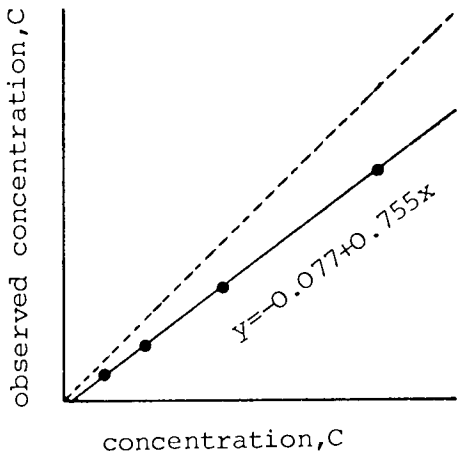
b) analysis of samples where C is taken over a range of concentrations

Some types of analytical error may show a functional relationship with concentration, ie they are relative rather than independent of concentration (B.S. 5497, 1979). The types of relationship are shown in Figure 5.1. Two error structures are illustrated; firstly, errors which are independent of concentration (5.1 (a) and (c)); and secondly, errors which are functions of concentration (5.1 (b) and (d)). In order to examine the error structure of the metal analysis procedure a range of concentrations were analysed. These were 0.5, 1.0, 2.0 and 4.0 µg/ml. Lead, copper and magnesium were analysed. Cadmium was not measured because the original cadmium hollow cathode lamp had been damaged. The results of these analyses are given in Table 5.6. From these results it is clear that for all three metals random error, σ_c is independent of concentration (within the range of concentrations used for this experiment) and therefore is best represented by Figure 5.1 (a).

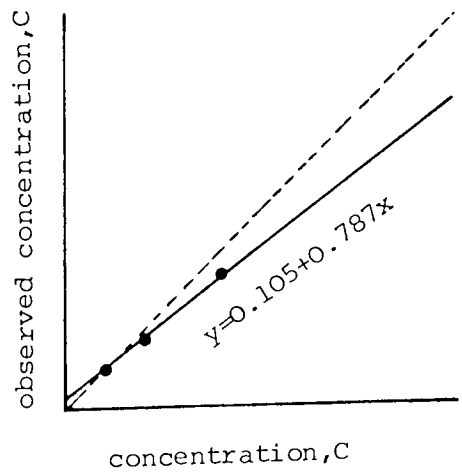
Analytical bias is shown by these results (Table 5.6) to account for a significant loss of metal. To illustrate how this loss varies with concentration, $\bar{c}$ has been plotted against C in Figure 5.2. In all cases the error structure is observed to be functional with concentration and is best described by Figure 5.1 (d). The structure of this bias can be further investigated using linear



a) Lead r^2=0.999



b) Copper r^2=1.000



c) Magnesium r^2=1.000

FIGURE 5.2 DETERMINATION $\bar{C}$ AGAINST TRUE CONCENTRATION C ILLUSTRATING THE BIAS STRUCTURE OF THE ANALYSES, (ug/g).

Table 5.6 Results of replicate analyses of samples of a range of concentrations C, n=6

	C	$\bar{c}$	σ_c	te
Lead	0.5	0.35	0.16	*
	1.0	0.72	0.15	**
	2.0	1.49	0.21	**
	4.0	2.84	0.15	**
Copper	0.5	0.30	0.13	**
	1.0	0.67	0.05	**
	2.0	1.45	0.11	**
	4.0	2.94	0.16	**
Magnesium	0.5	0.50	0.03	
	1.0	0.89	0.06	**
	2.0	1.68	0.06	**

* te 5% = 2.015 ** te 1% = 3.365

regression analysis (Yeomans, 1968). The appropriate regression equations are shown in Figure 5.2. These equations can be used to examine whether all of the observed bias is relative to concentration or fixed (ie independant of concentration). The breakdown of these two error components is given in Table 5.7. For lead there is evidence of a fixed bias of 0.017 ug/ml and a relative bias of 0.289•x (where x is the known concentration C).

These results clearly demonstrate that the vast majority of the observed bias is relative bias rather than fixed bias and this produces a constant under-estimation of the true concentration of 29%: ie only 71% of the lead has been recovered.

The regression breakdown can also be used to provide estimates of the random error or precision for all concentrations. The residual sum

Table 5.7 Fixed bias, relative bias and random error for lead analysis

True Concentration	Estimated error due to fixed bias	Estimated error due to relative bias (0289 x)	Estimated total error due to bias (fixed& relative)	Predicted determination	Measured concentration	Residual (estimated) random error	Residual squared
0.5	0.017	0.145	0.162	0.373	0.35	-0.02	0.0004
1.0	0.017	0.289	0.306	0.728	0.72	-0.01	0.0001
2.0	0.017	0.578	0.595	1.439	1.49	0.05	0.0025
4.0	0.017	1.156	1.173	2.861	2.84	-0.02	0.0004
						0.00	0.0034

of squares can be used to calculate the residual variance, 0.0034/n-2 which gives 0.0017 (Goodall, 1983). The standard deviation σ_c can be calculated from this by $\sqrt{0.0017}.\sqrt{6} = 0.10$. Compared to the previous estimate of σ_c of 0.11, obtained from a) above, it appears that analytical error is constant between the two experiments.

As a final point it should be noted that these estimates of analytical error are derived from synthetic samples. These samples are, as far as possible, matrix matched against those of deposition samples. However, the presence of interfering elements such as sodium, calcium, and magnesium may increase analytical error for samples where they are found in high concentrations (Waughman and Brett, 1980).

5.3.3 Resolution of errors of individual component stages

The analytical process consists of four clearly identifiable stages

1 Sample preparation

2 acid digestion

3 solubilization

4 determination

Analytical errors arising in each of these stages would be expected to combine according to the Theory of Addition of Errors (Crumpler, 1946 and Clifford, 1973). By introducing replicate blank control samples at each of these four stages of the analytical procedure, estimates of random error and bias have been obtained. The results of these blank analyses are given in Table 5.8. The mean concentration observed in the replicated samples is indicated as $\bar{c}_i$, and the error

TABLE 5.8 Breakdown of random error and systematic error for each of the five analytical stages compared to the total measurement error σ_c.

	σ_c	Evaporation i=1 n=6			Digestion i=2 n=6			Solubilization i=3 n=6			Determination i=4 n=7		
		$\bar{c}_1$	σ_1	$\frac{F}{t}$	$\bar{c}_2$	σ_2	$\frac{F}{t}$	$\bar{c}_3$	σ_3	$\frac{F}{t}$	$\bar{c}_4$	σ_4	$\frac{-}{t}$
LEAD	0.11	0.10	0.33	$\frac{**}{--}$	0.06	0.16	$\frac{**}{--}$	0.02	0.09	$\frac{**}{--}$	0.01	0.02	--
CADMIUM	0.02	-0.08	0.13	$\frac{**}{--}$	0.01	0.01	$\frac{-}{*}$	0.01	0.03	$\frac{**}{--}$	0.02	0.003	$\frac{--}{**}$
Aluminium	0.16	0.58	0.29	$\frac{--}{**}$	2.24	1.14	$\frac{**}{**}$	0.27	0.14	$\frac{--}{**}$	0.20	0.14	$\frac{--}{**}$
Arsenic	0.02	0.01	0.01	--	0.12	0.01	$\frac{--}{**}$	0.02	0.003	$\frac{--}{**}$			
Chromium	0.24	0.02	0.02	-	-0.06	0.04	$\frac{-}{*}$	0.02	0.06	$\frac{*}{--}$	-0.01	0.02	--
Copper	0.04	0.04	0.01	$\frac{--}{**}$	0.08	0.06	$\frac{**}{*}$	0.03	0.07	$\frac{**}{--}$	0.00	0.01	--
Iron	0.05	0.21	0.26	--	0.26	0.21	$\frac{--}{*}$	0.20	0.45	--	0.23	0.26	--
Magnesium	0.05	0.22	0.04	$\frac{--}{**}$	0.33	0.16	$\frac{**}{**}$	0.13	0.05	$\frac{*}{**}$	0.00	0.02	--
Manganese		0.02	0.02	-	0.01	0.01	$\frac{*}{--}$	0.02	0.02	--	-0.01	0.03	--
Zinc	0.43	0.22	0.23	$\frac{**}{--}$	4.39	2.47	$\frac{**}{**}$	0.06	0.10	$\frac{**}{--}$	0.00	0.01	--

* p=0.05 ** p=0.01

standard deviation by σ_i, where $_i$ is the analytical stage. The error associated with detection (atomic absorption spectrophotometry) will represent the minimum error possible, therefore an F test is used to test whether the random error σ_i at each preceding stage is statistically significantly greater than that of detection, σ_4. The t-test has been used to test if the replicate sample mean, $\bar{c}_i$ is significantly different from zero (ie the test is used to detect bias).

These results show the random variance for lead is significantly greater (99% probability level) at all stages in the analysis compared to the random error of atomic absorption determination. There is no evidence of significant bias at any stage of the analytical process. For Cadmium on the other hand random error is significantly increased during solubilization and preparation and there is some evidence of bias at the digestion stage.

These results would suggest that the analytical precision could be significantly improved by reducing the error involved in sample pretreatment (see Minczewski, 1982).

For other metals, arsenic, chromium, iron and manganese, analytical precision could be improved by increasing the signal/noise ratio of the detection instrument. This is considered in Appendix B.3 and by Liteanu and Rica (1980). Improvements could also be obtained by using a more sensitive analytical detection system, eg Neutron activation analysis or flameless atomic absorption (Pinta 1962).

5.4 Summary and conclusions relating to the deposit cannister measurement method

5.4.1 Measurement error

The experimental investigation of the measurement error of the deposit cannister has provided estimates of the precision of the method. Measurement error has been found to be of broadly similar magnitude in two areas of contrasting environmental conditions. However, more rigorous testing is required to enable the measurement error to be characterised for a broader range of environments not covered in this study. The main survey (Survey 1) in this research has used a sample density of one cannister per site; however other studies more concerned with obtaining precise estimates of deposition rates at individual sites, will probably require a higher sample density.

5.4.2 Analytical errors

The analytical error, σ_c has been quantified and found to be independant of the concentration of metal in solution within the linear range of the analytical response function. Bias on the other hand tends to increase with concentration. For both lead and cadmium the sample pretreatment process prior to determination contributes significantly to background analytical noise but not to the levels of contamination within analytical blanks. This suggests that the sample pretreatment process increases detection interference but not through contamination. However, for other metals such as aluminium, arsenic and magnesium there is significant sample contamination during pretreatment.

5.4.3 Instrument errors

Having experimentally obtained values of σ_m and σ_c it is possible to derive an estimate of instrument error, σ_I using the principle of addition of variances. Firstly however, the estimates of σ_c must be converted into units of $mg/m^2/30d$ using the conversion factor of 0.331. This gives values of σ_c of $0.063 mg/m^2/30$ d for lead amd 0.012 $mg/m^2/30d$ for cadmium. Therefore, the resolution of error components for the deposit cannister method gives σ_I for lead of:-

$$\sigma_I = \sqrt{\left(\sigma_m^2 - \sigma_c^2\right)}$$

$$= \sqrt{0.123^2 - 0.063^2}$$

$$= \underline{0.106 \text{ mg/m}^2/30d}$$

and estimates of σ_I for cadmium of:

$$\sigma_I = \sqrt{0.015^2 - 0.012^2}$$

$$= \underline{0.009 \text{ mg/m}^2/30d}$$

Thus for lead analytical error explains only 26% of the error variance associated with deposition measurement while for cadmium analytical errors are more important in determining precision to which deposition can be measured, explaining 64% of the error variance of deposition measurement.

5.4.4 Conclusions

The deposit cannister technique is sufficiently cheap and flexible to allow high sample densities to be used at low cost and without

the difficulties involved in siting large numbers of deposit gauges in confined areas. The relative accuracy of the deposit cannister technique and the deposit gauge method have not been evaluated. A general evaluation of the precision of the two methods for lead deposition measurement suggests that the measurement error of the deposit cannister is of a similar order to that of the more rigorously tested standard ISO gauge.

The deposit cannister therefore represents an effective means for monitoring deposition on a large scale in areas where such surveys have been previously technically and practically impossible. It therefore satisfies the requirements of this research project.

CHAPTER 6

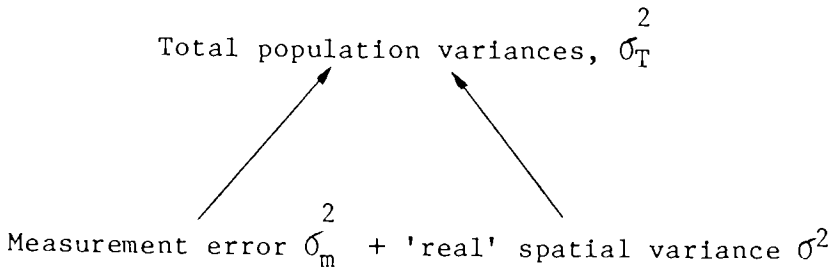
6. ANALYSIS OF RESULTS; GENERAL LEVELS AND SPATIAL VARIABILITY OF DEPOSITION IN WALSALL

6.1 Introduction

6.1.1 Outline

This chapter examines the results of deposition surveys 1 and 2 and aims to provide detailed information on the general levels and spatial variability of lead and cadmium deposition rates within the study area (Ob.2).

The sample framework for survey 1 has been considered in Section 4; to summarise, this consisted of a large number of deposition measurements grouped into $1km^2$ sample squares chosen to provide a cross-section of the urban and non-urban environments present in the study area. The 250 deposition measurements will represent a sample taken from a theoretically infinite number of possible deposition measurement sites within the borough area which themselves represent a statistical population. The mean and standard deviation of the deposition measurements will represent estimates of the total population mean and standard deviation, providing that the measurements are independent and random (Chatfield, 1978). The standard deviation of the deposition measurements σ_T, will depend on the spatial variability of deposition occurring between measurements sites and the error involved in measuring deposition using the deposit cannister, σ_m (from section 5.2). According to the principle of addition of variances, this relationship can be represented by:



This chapter aims to estimate the percentage of total variance explained by spatial variation at three different scales; the location taken as an area of $100m^2$; the area taken as $1Km^2$ grid sample area; and the urban area at a scale of approximately $10Km^2$.

Apart from the analysis of spatial variance, the data on deposition obtained during survey 1 are useful in that they allow a detailed investigation of the levels of deposition found in an urban area to be carried out. This investigation has two aspects; firstly an evaluation of the potential environmental significance of the general levels of lead and cadmium deposition in Walsall, and secondly an examination of the geographic pattern of the distribution of lead and cadmium deposition rates across the Walsall Borough area generally.

6.1.2 Structure of the Chapter

Section 6.2 discusses the results of survey 1 and examines the levels of deposition of lead and cadmium in Walsall compared to surveys conducted in other urban areas and the F.D.R deposition standards. Section 6.3 goes on to consider the nature of spatial variability of deposition in urban areas and derives estimates of the spatial variance at different spatial scales. Section 6.4 provides a summary of main conclusions of Chapter 6.

6.2 Levels and geographic distribution of lead and cadmium in deposition in Walsall

6.2.1 Results of survey 1

Walsall has been shown to have elevated levels of lead and cadmium in soil (Pocock, 1982). Cadmium levels in particular have been a cause for concern and have prompted an investigation of the potential human exposure in the Walsall area (Tennant, 1984). Deposition is a potentially important input pathway to soils and the human food chain through the pollution process detailed in Chapter 1. This section examines the levels of deposition of these metals in the Walsall area, in comparison firstly with the levels observed in urban areas and secondly the deposition standards used in the F.D.R (Weber, 1981).

The results obtained during survey 1 form a statistical population of measurements with mean $\bar{x}$ and standard deviation σ_T. The individual sample site results are listed in Appendix D. Table 6.1 contains a summary of these results based on arithmetic statistics. For lead the arithmetic mean deposition rate is 2.20 mg/m^2/30d and the standard deviation exceeds the mean by a factor of 2. The range of observations covers 4 orders of magnitude from 0.03-51.4 mg/m^2/30d. For cadmium the arithmetic mean deposition rate is 0.07 mg/m^2/30d and the standard deviation is approximately equal to the mean. Cadmium deposition ranges from 0.01 to 0.64 mg/m^2/30d. The comparatively large standard deviations and large range of deposition rates (in both cases the upper values exceed $3\sigma_T$) suggest that the data is skewed from the normal distribution (Aitchison and Brown, 1957). The frequency distributions in figure 6.1 (a) and (b) for both metals in fact show marked positive skew (skew to

Table 6.1 Statistical summary of survey 1 results based on the arthmetic scale $mg/m^2/30$ days

	Valid observation N	Mean $\bar{X}$	standard deviation σ	range min-max	95% confidence interval For mean
Lead	196	2.20	4.31	0.03-51.4	1.59-2.80
Cadmium	184	0.07	0.07	0.01-0.64	0.06-0.08
Aluminium	199	10.0	6.7	1.8-47.3	9.0-10.9
Arsenic	192	0.0033	0.015	0.010-0.095	0.031-0.035
Chromium	183	0.24	0.34	0.01-3.55	0.19-0.29
Copper	197	2.93	6.31	0.04-68.7	2.04-3.81
Iron	198	22.4	24.8	1.4-183.8	18.9-25.9
Magnesium	197	6.4	4.7	0.40-29.9	5.7-7.0
Maganese	197	1.22	1.47	0.05-11.40	1.01-1.42
Zinc	192	39.7	40.2	1.6-389.5	31.0-45.4

the right). This is seen also in the frequency distribution for the remaining eight metals given in Appendix D. This positive skewness is reduced by employing a logarithmic transformation of the data ($\log_{10}X$). This is illustrated by the probability distributions plotted on log-probability paper in Figures 6.2 and 6.3. The data points lie approximately on straight lines indicating a good approximation of a log-normal distribution (test detailed by Aitchison and Brown 1957). The descriptive population statistics based on log-normalised data are given in Table 6.2.

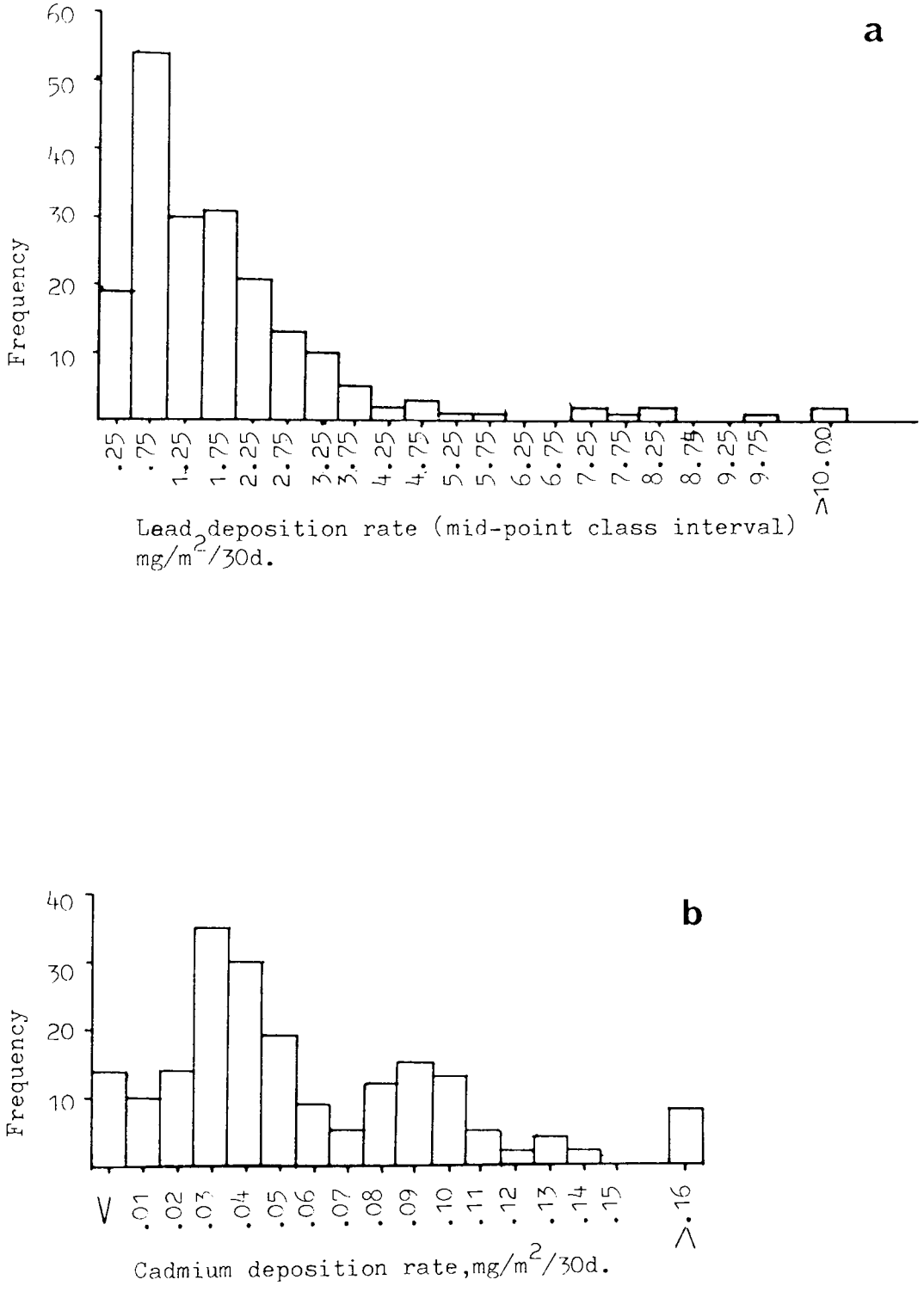


FIGURE 6.1 FREQUENCY DISTRIBUTIONS FOR LEAD AND CADMIUM DEPOSITION IN SURVEY 1, a) Lead and b) Cadmium.

Taking the antilog of these statistics gives geometric means and 95% probability ranges (a convienient method of expressing the geometric standard deviation). The resulting geometric mean for lead equals 1.38 mg/m^2/30d with a 95% probability range of 0.23-8.11mg/m^2/30d, and for cadmium equals 0.05 mg/m^2/30d with a 95% probability range of 0.01-0.21 mg/m^2/30d. These statistics are better desciptive expressions of the data than those based on the arithmetic scale which are biased by the positive skew.

Table 6.2 Statistical summary of survey 1 results log scale (log. mg/m^2/30d)

	Valid observation N	Mean $\bar{X}$	standard deviation σ	range min-max	95% confidence interval For mean
Lead	196	0.139	0.385	-1.52-1.711	0.084-0.193
Cadmium	184	-1.305	0.317	-2.00-0.194	-1.351--1.259
Aluminium	199	0.919	0.260	0.255-1.675	0.882-0.955
Arsenic	192	-1.520	0.179	-2.00-1.022	-1.545--1.494
Chromium	183	-0.806	0.399	-2.00-0.550	-0.864--0.748
Copper	197	0.163	0.470	-1.398-1.837	0.097-0.229
Iron	198	1.181	0.378	0.146-2.264	1.128-1.234
Magnesium	197	0.715	0.280	-0.398-1.476	0.676-0.755
Maganese	197	-0.109	0.402	-1.301-1.057	-0.165--0.052
Zinc	192	1.427	0.400	0.204-2.591	1.371-1.484

While data transformations are of specific value where statistical tests require statistical data normality of the data set, there are considerable disadvantages in transforming data. The main disadvantage is that the re-expression involves a measurement scale that is often less familar and intuitively less easy to understand and interpret (Emerson and Stoto, 1983). However, in some cases transformation can be achieved without scale alteration (as for example with the geometric mean which are equivalent to the logtransformed mean). Wherever possible geometric means are used in this research, particularly for presenting area-based deposition averages, in order to maintain statistical validity.

6.2.2 Sample-square area mean deposition rates

The 249 measurement sites in deposition survey 1 were grouped into twenty-seven $1Km^2$ areas, at a density of nine cannisters per $1Km^2$. The mean deposition rates observed in the sample squares are also lognormally distributed. This is illustrated by the logarithmic standard deviation range plots given in Figure 6.4 (a) and (b) where the mean and standard deviation are calculated on a logarithmic scale but presented against the equivalent arithmetic scale to aid interpretation. The standard deviation is seen to be independent of the sample square mean deposition rate. These two plots also show that while the standard deviation is relatively constant, variability in terms of the arithmetic scale tends to increase as sample square mean increases. This generally supports the conclusion drawn in Section 2.6.1: that spatial variability is highest near to point sources and in urban areas.

FIGURE 6.2 LOG PROBABILITY DISTRIBUTION FOR LEAD DEPOSITION RATES

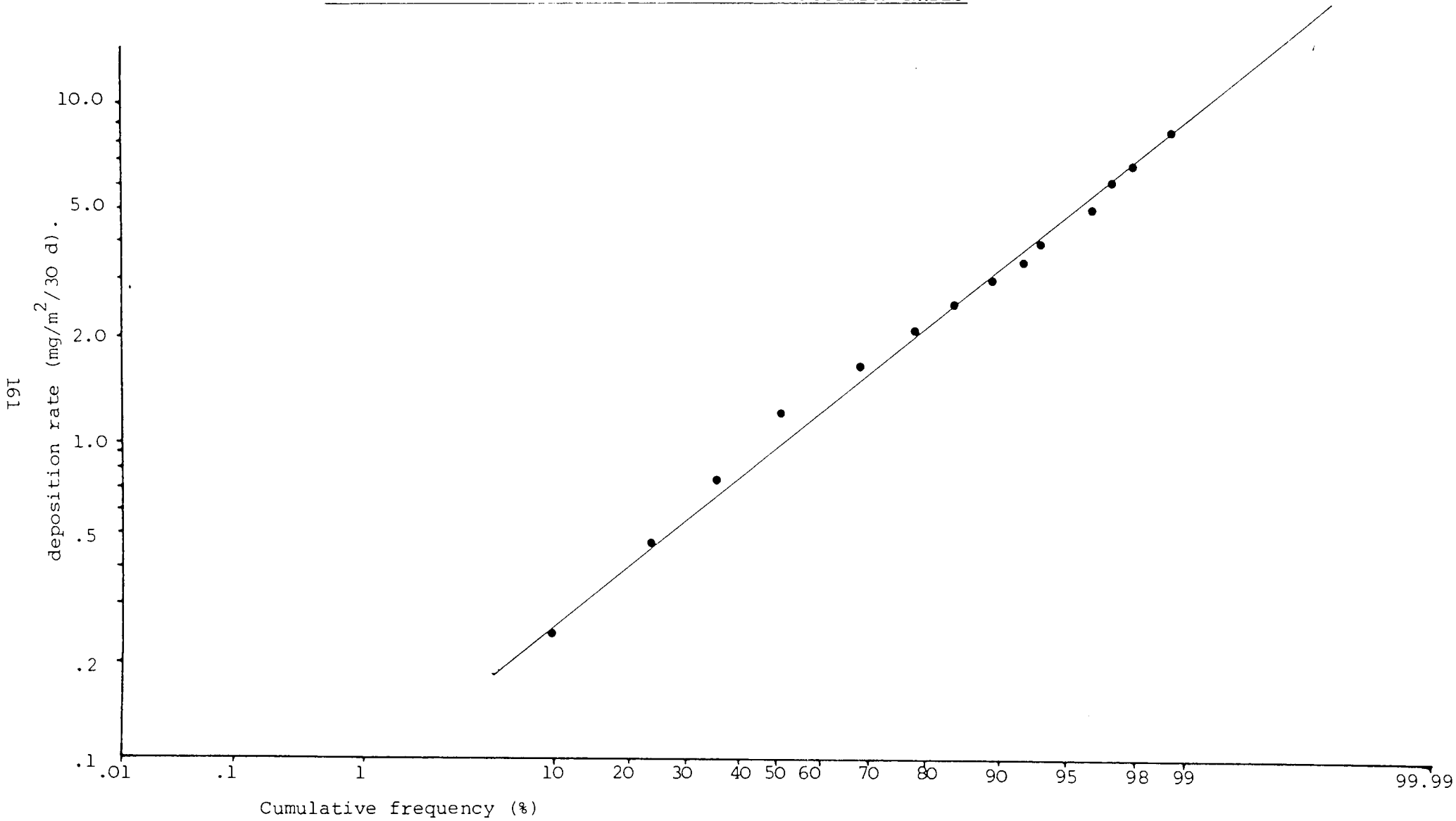
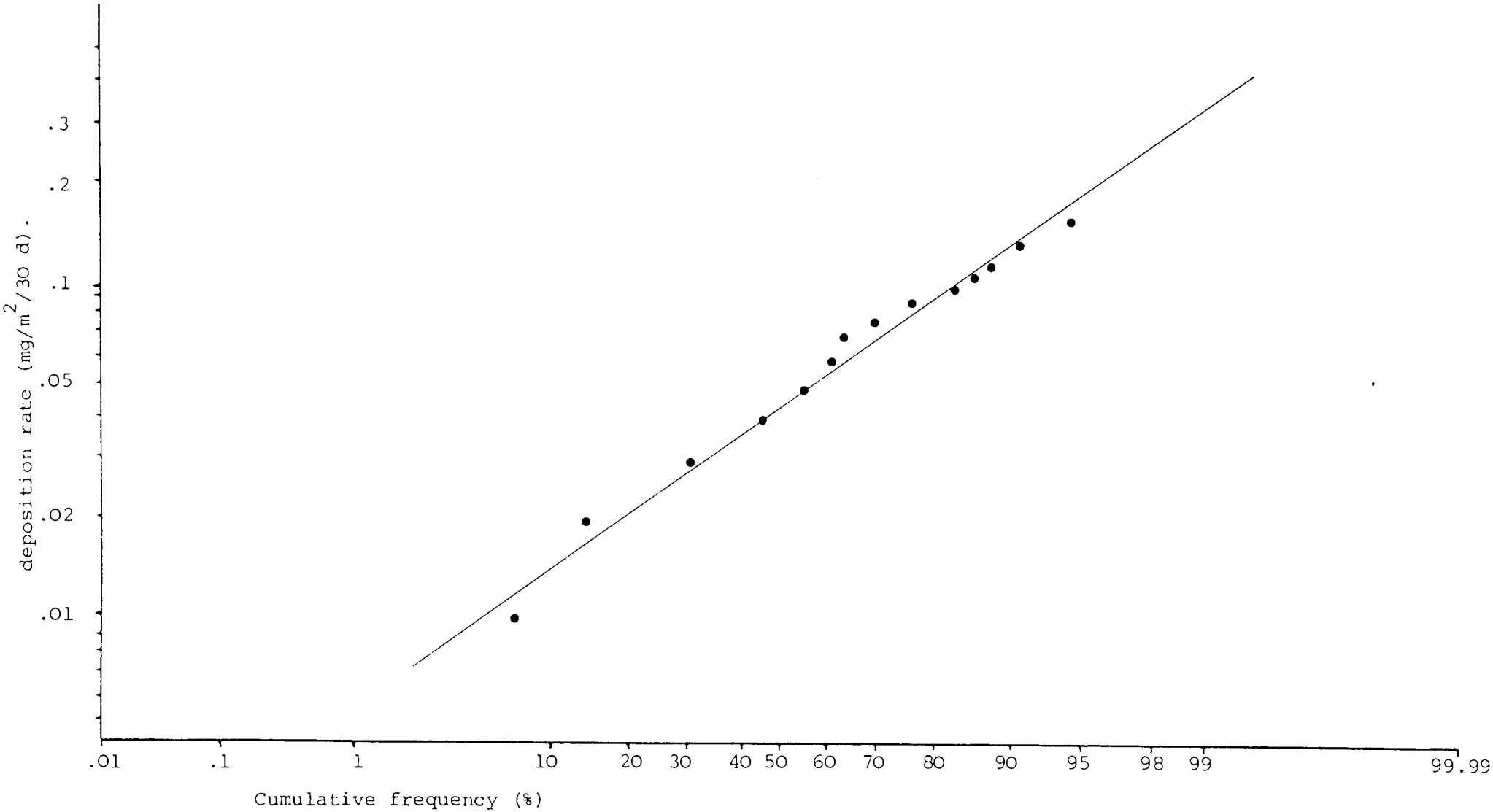


FIGURE 6.3 LOG PROBABILITY DISTRIBUTION FOR CADMIUM DEPOSITION RATES



The geographic pattern of the distribution of the sample square geometric mean deposition rates is mapped out in Figure 6.5 and 6.6. From these figures it can be seen that for both lead and cadmium the central urban area of Walsall has generally higher levels of deposition than the western or eastern edges of the borough. The lowest lead deposition rates of 0.6 mg/m^2/30 days and cadmium deposition rates of 0.02 mg/m^2/30 days occur in the south eastern part of the borough which is characterised by open rural areas and low density residential areas. The highest average lead deposition rates of 4.6 mg/m^2/30d occur in a dense urban/ industrial area next to the M6 motorway and near to a secondary copper refinery. The highest cadmium deposition rate of 0.11 mg/m^2/30d is recorded in two adjacent squares in an urban/industrial area characterised by a high density of metal works (including secondary lead recovery, iron founding, brass founding and galvanizing). The relationship between sources and the geographic distribution of deposition is examined in detail in Chapter 7.

6.2.3 Comparison between deposition rates in Walsall and those measured in other urban areas

The typical levels of lead and cadmium deposition in urban areas have been summarised in Table 2.3. The average levels of lead and cadmium observed in this study are typical of those reported for urban areas. Lead deposition is at the lower end of the reported range. This unexpected finding (Walsall being relatively polluted) is possibly due to the siting policy adopted in previous deposition studies, where monitoring sites are placed in situations of high deposition, these being areas of most immediate concern. In this

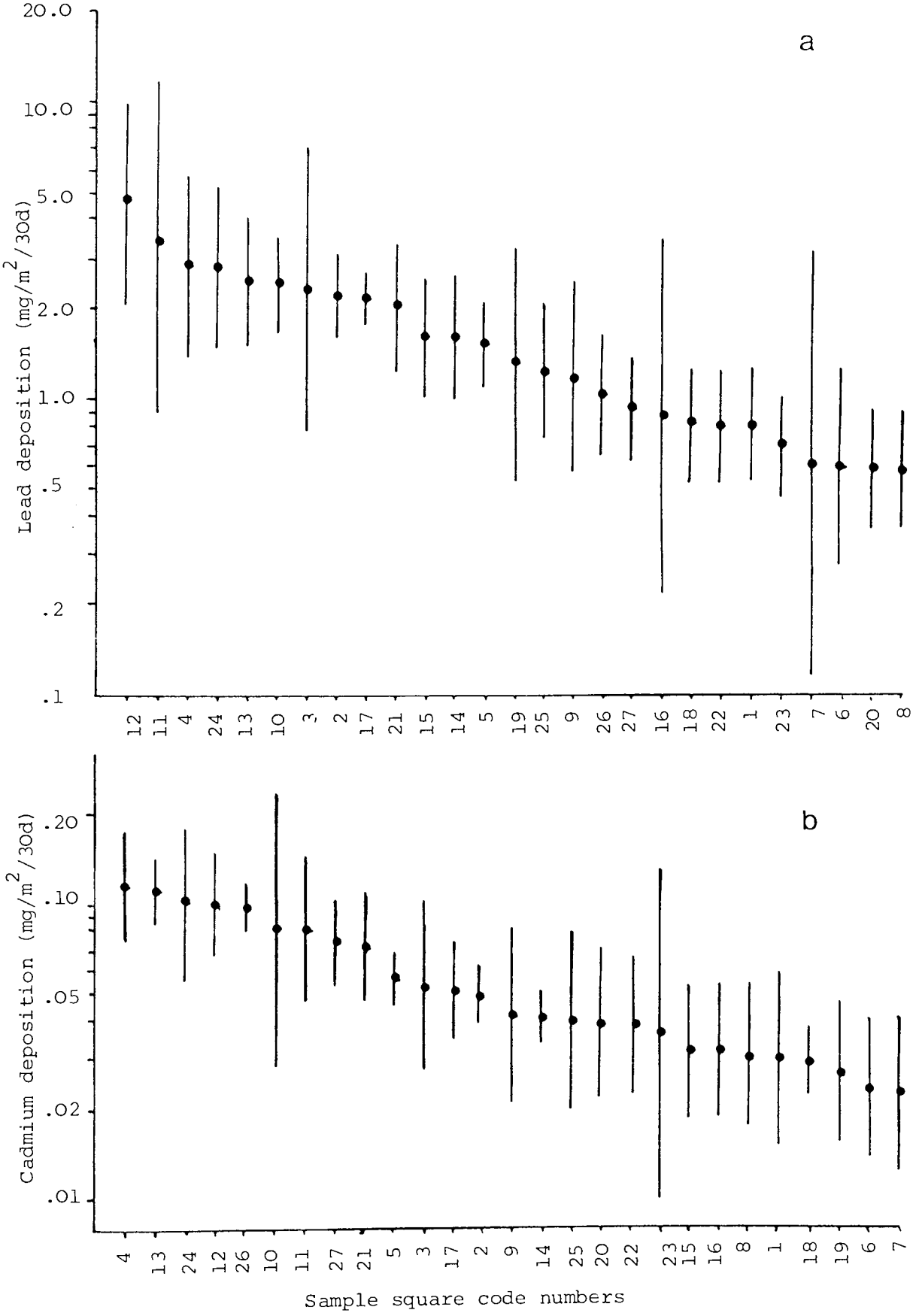


FIGURE 6.4 SAMPLE SQUARE LOG MEAN AND STANDARD DEVIATION RANGE

(a)Lead deposition rates & (b)Cadmium deposition rates.

FIGURE 6.5 GEOMETRIC MEAN LEAD DEPOSITION RATES FOR SAMPLE SQUARES IN SURVEY 1.

Geometric mean lead deposition ($mg/m^2/30d$).

2·5

0 1 2 kilometres

Content has been removed for copyright reasons

FIGURE 6.6 GEOMETRIC MEAN CADMIUM DEPOSITION RATES FOR SAMPLE SQUARES IN SURVEY 1.

Geometric mean cadmium deposition ($mg/m^2/30d$).

·03

0 1 2 kilometres

N

Aston University

Content has been removed for copyright reasons

survey which is an ambient survey, a large number of sites have been monitored, many of which would not typically be included in more limited studies (eg many sites are in sub-urban/rural areas). Thus if the survey had concentrated on the central urban area around Walsall town centre, the survey mean would be expected to be more of the order of 3-5 $mg/m^2/30$ days (as shown in Figure 6.5) which would be more typical of deposition in central London (eg Harrison et al, 1975 and Duggan and Burton, 1983).

Average cadmium deposition in Walsall compares with the higher values reported for cities. Bearing in mind the point raised in the preceding paragraph, it is likely that on balance cadmium deposition is slightly elevated in Walsall compared to other urban areas.

6.2.4 Comparison with the deposition standards used in West Germany

The deposition standards employed in the F.D.R have been described in Section 2.5. These standards relate to typical long-term deposition rates measured using the ISO type of deposit gauge. In this study deposition measurements for a single month are available and there are obvious questions over the long-term representativeness of a single winter time sample period. In addition, the relative collection efficiencies of the ISO deposit gauge and the deposit cannister are not yet known and therefore the relevance of the F.D.R standards to deposit cannister measurements is obviously questionable. However, despite these difficulties the F.D.R standards can still be used to gain an approximate estimate of the potential environmental significance of the observed deposition rates (Pocock and Simmons, 1984). This can be achieved by using the log probability distributions given

in Figure 6.2 and 6.3 and 'reading off' the proportion of sites exceeding given levels. For example the mean of the population can be estimated using the fitted straight line to find the value of deposition whose estimated cumulative frequency is 50%. The results of this procedure when applied to the F.D.R standards are summarised in Table 6.3 which shows that there is a much larger proportion of sites which exceed the cadmium standards compared

Table 6.3 Percentage of Walsall deposition survey sites exceeding BIm SchG Deposition rate standards

	Pb	Cd
Maximum.	0.3%	4.0%
Fish, fruit and Vegetable Cultivation.	1.8%	32.0%
Grazing of cattle,sheep and pigs.	0.3%	32.0%

to those exceeding the lead standards. The maximum lead and cadmium deposition rates of 51.4 and 0.64 mg/m^2/30d respectively are each some three times higher than the maximum standard. A further salient point is that this research focuses on ambient deposition levels; no attempt has been made to monitor 'hotspots' (indeed, busy roadsite sites were specifically avoided). It may be concluded however that the vast majority of sites in the Walsall area are well within the maximum standards for lead. For cadmium however, the evidence suggests that there is a much more widespread incidence of standards being exceeded and this observation may be of signifiance given the extent of garden and allotment cultivation in the urban

part of the borough (Tennant, 1984). It must be stressed again that these results should be treated with some caution pending further investigation of the deposit cannister.

6.3 Analysis of the spatial variation of deposition levels in urban areas

6.3.1 Spatial scales and variance

The preceding section has examined the levels of lead and cadmium deposition in survey 1 and their geographic distribution. This section presents a detailed statistical analysis of the spatial variation of deposition and attempts to explain the total population variance, σ^2_T observed in in survey 1, in terms of spatial variance at three spatial scales, the location, area and urban area.

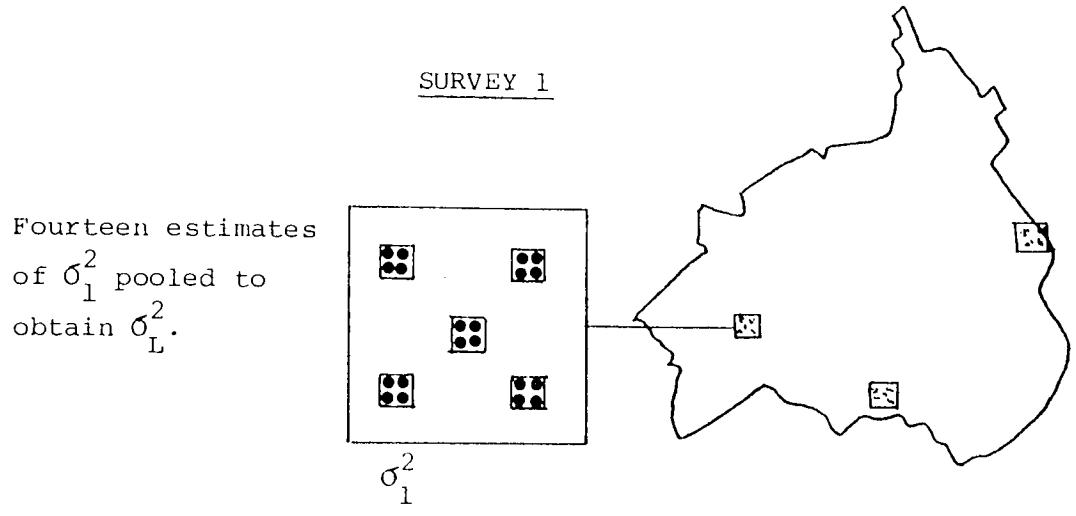
Estimates of the total variation observed in survey 1 have been derived in Section 6.2.2. This section considers variance σ^2_T in the log transformed population, therefore the relevant estimates of σ^2_T are given by the squares of the standard deviations given in Table 6.2. These variances represent the sum of variances arising from real spatial variations in deposition that occur between measurement sites, added to the variance attributable to measurement error. From purely practical considerations (ie available siting positions) three levels of spatial variances have been selected for study, these are represented as:-

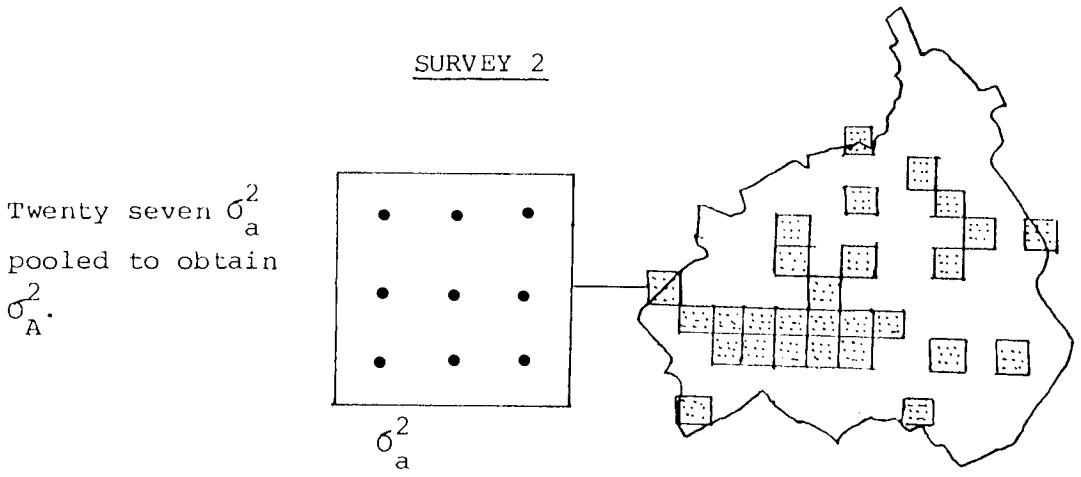
- location variance, σ^2_L ($100m^2$ area)
- area variance, σ^2_A ($1000\ m^2$ area)
- urban-scale variance, σ^2_U ($10Km^2$ area).

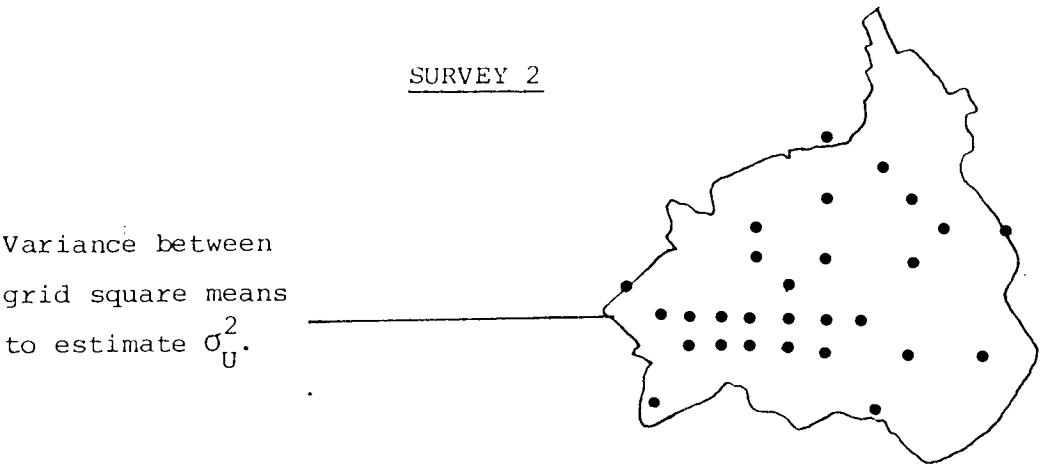
In theory, the interrelation of these variance is described according to the principle of addition of variances by

$$\sigma^2_T = \sigma^2_m + \sigma^2_L + \sigma^2_A + \sigma^2_U$$

FIGURE 6.7 DIAGRAMMATIC REPRESENTATION OF THE PROCEDURE FOR ESTIMATING σ_L^2, σ_A^2 AND σ_U^2.







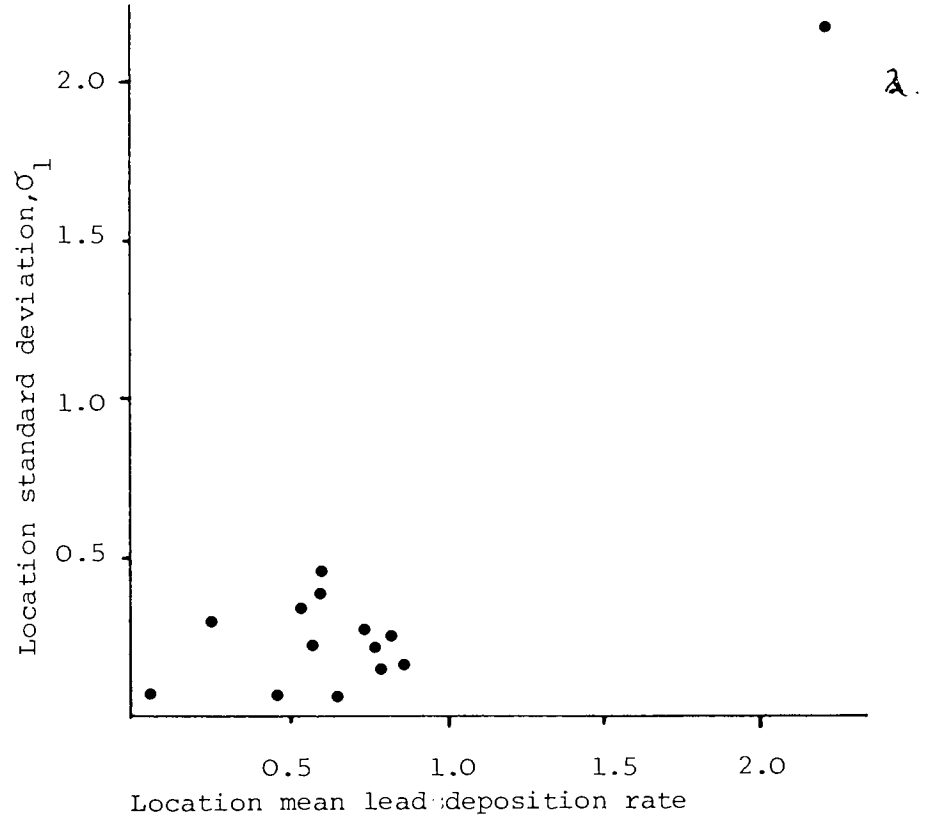
Estimates of measurement error σ_m have been derived in section 5.2 as 0.12 mg/m^2/30 days for lead and 0.015 mg/m^2/30d for cadmium. The discussion now centres on estimating the three levels of spatial variation.

6.3.2 Estimating spatial variances

The two deposition surveys 1 and 2, together allow estimates of spatial variance to be calculated. Survey 2 was specifically designed to examine the small-scale spatial variation and survey 1 can be used to give estimates of larger scale spatial variation. The design of these two surveys has been described in section 4. Figure 6.7 shows how these surveys may be used to obtain the estimates of spatial variance at the different scales.

a) Location variance

Survey 2 incorporated fourteen clusters each of four deposit cannisters, each cluster being located within a 100m^3 area (the location). Five of these locations were taken from an urban area, five from a residential area and four from a rural area. By stratifying the sample in this way the 'location variance' can be examined over a range of typical urban environments. The results of these fourteen cluster groupings are given in Table 6.4. The pooled estimate of the within-location variance, σ^2_L is derived as the arithmetic average of the separate location variance estimates. The plots of location standard deviation against location mean given in Figure 6.8 (a) and (b) generally show that the variability of deposition rates within a location and the mean levels at that location are independent; therefore the pooling of variances is statistically valid.



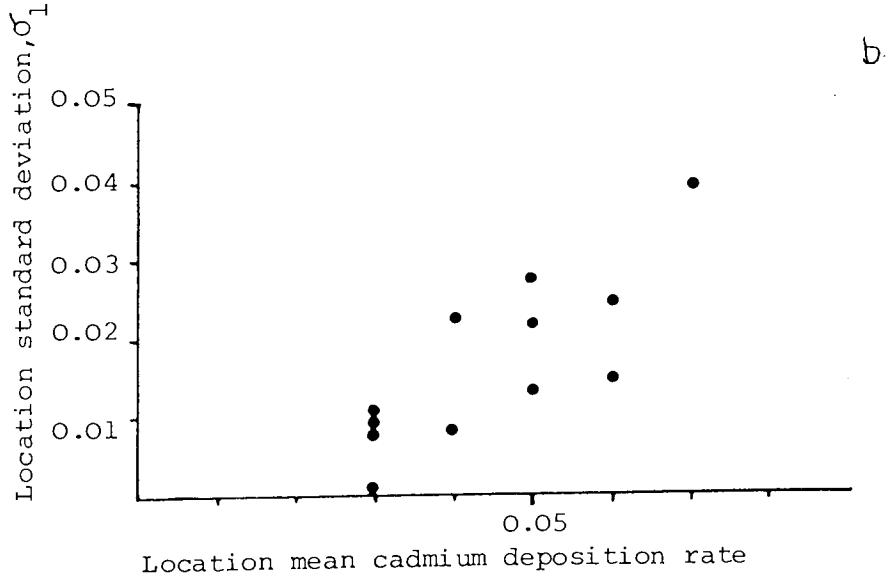


FIGURE 6.9 LOCATION STANDARD DEVIATION PLOTTED AGAINST LOCATION MEAN DEPOSITION RATES($mg/m^2/30d$), a) Lead and b) Cadmium.

Table 6.4 Summary of location variance estimates σ^2 and location mean deposition rates, ($mg/m^2/30d$).

	Lead		Cadmium	
	Location mean	Location standard deviation σ_L	Locaton Mean	Location standard deviation σ_L
1	0.60	0.39	0.05	0.028
2	0.67	0.05	0.03	0.007
3	0.86	0.14	0.04	0.008
4	2.23	2.21	0.05	0.012
5	0.76	0.13	-	-
6	0.58	0.24	0.03	0.000
7	0.72	0.27	0.04	0.012
8	0.49	0.09	0.03	0.007
9	0.76	0.21	0.06	0.015
10	0.79	0.24	0.5	0.025
11	0.59	0.44	-	-
12	0.53	0.35	0.07	0.040
13	0.29	0.27	0.05	0.014
14	0.04	0.03	0.03	0.009
	$\bar{X}$ 0.71		$\bar{X}$ 0.044	
pooled estimate of standard deviation:		0.64		0.018

However these two estimates of pooled variance will contain an component of variance attributable to measurement error. This can be isolated from the true spatial variation by:-

$$\text{'true'}\ O2_L = O2_L - O2_m$$

For lead this gives the true location variation as σ_L = 0.628 mg/m^2/30d and the true location variation for cadmium as σ_L = 0.010 mg/m^2/30 d.

b) Area variance and urban scale variance

Estimates of both σ^2_A and σ^2_U can be dervied from the results of survey 1. These two components of variance can be isolated using the statistical technique of analysis of variance (ANOVA) which aims to isolate the variance due to within-group variation from that arising from differences between groups. The results of the analysis of variance for lead and cadmium are summarised Tables 6.5 and 6.6.

Table 6.5 Analysis of variance for lead deposition rates performed on logtransformed data

Source of variation	sum of squares	degrees of freedom	mean square	F ratio
between group	12.9981	26	0.4999	5.311**
within group	15.9084	169	0.0941	
total	28.9065	195		

** F Significant at 1%

The within-group mean squares are estimates of σ^2_A since these represent the variance due to variations between the measurements in each sample area (1Km^2).

Table 6.6 Analysis of variance for cadmium deposition rates performed on logtransformed data

Source of variation	sum of squares	degrees of freedom	mean square	F ratio
between group	8.3535	26	0.3213	5.046**
within group	9.9956	157	0.0637	
total	18.3491	186		

** F Significant at 1%

The analysis of variance also provides a means of testing whether the observed differences between sample square mean deposition rates are significantly greater than differences that would be expected to occur entirely as a result of the random within-square variability, (ie is $\sigma^2_U = 0$?) This equates to the hypothesis that deposition levels vary between different types of urban area. An F test is used to test this hypothesis. In both cases the between-sample-square variation is highly significantly different from zero (at 99% probability level)[1]. Having confirmed that the between group variance is certainly not equal to zero the between group mean square can be used to estimate σ^2_U, but since both between-sample-square variability and within-square variability have contributed to this mean square, the estimate of σ^2_U is given by:-

$$\sigma^2_U = \frac{\text{(between group mean square - within group mean square)}}{\text{mean number of measurements per group.}}$$

(Caulcutt and Boddy 1983)

1. The analysis of variance requires that data have homogeneity of variances and fit the Normal distribution. In this survey both of these assumptions are satisfied only by log-normalised data. Although an analysis of variance on untransformed data does show a significant F value, the variance within a grid square would be overestimated. (Aitchison and Brown, 1957)

The estimate of within group variability, σ^2_A contains not only area variance but also the components of location variance σ^2_L and measurement error, σ^2_m which have both been estimated from the original measurements, and so have a unit scale of $mg/m^2/30d$. The estimates of σ^2_A and σ^2_U have both been obtained from a unit scale of log $(mg/m^2/30d)$ and as such are incompatible. However to aid interpretation it is possible to calculate the standard deviation range (population mean $\pm$ standard deviation). These results of the spatial analysis are given in Table 6.7, from which it can be seen that 67.3% of the total variance of lead and 63.4% of the total variance of cadmium is accounted for by variance <u>within</u> the sample squares. The most significant source of variance within the sample square is that of <u>area variance</u>, ie variations in deposition occuring over an area scale of $1Km^2$. For lead, location variance is also important. Large scale urban area variance accounts for 32.7% of total variation for lead and 36.6% for cadmium. Thus it may be concluded that in an urban area the small scale ($>$ 1Km) variations in deposition are more significant than the larger scale differences between urban environments. This has important implications for deposition monitoring survey design and strengthens the argument that high spatial sampling densities are needed in order to obtain representative results (see 6.3.4 below).

6.3.3 <u>Spatial distribution of 'hotspot' deposition (survey 3)</u>

The results and discussion of the source - hotspot deposition survey using a flat snow surface to collect deposition are reported in full in Appendix C. This investigation (survey 3) has confirmed that deposition in the vicinity of sources follows an exponential distance-decline and approaches background within a kilometre. The bulk of hotspot

Table 6.7 Results of the investigation of spatial variance of lead and cadmium deposition

	Measurement error	Location variation	Area Variation	Urban area variation	Total variation
	$mg/m^2/30d$		$\log(mg/m^2/30d)$		
Lead σ	0.123 (1.500-1.254)	0.628 (2.0.005-0.749)	0.307 (2.792-0.679)	0.241 (2.398-0.790)	0.385 (3.341-0.567)
% of variance explained	← 67.3% →			32.7%	100%
Cadmium σ	0.015 (0.065-0.035)	0.010 (0.060-0.0.040)	0.252 (0.088-0.028)	0.192 (0.076-0.032)	0.317 (0.103-0.024)
% of variance explained	← 63.4% →			36.6%	100%

Figure in brackets are standard deviation ranges computed from:

upper bound = antilog (population mean + standard deviation)
lower bound = antilog (population mean - standard deviation)
or upper bound = population + standard deviation
lower bound = population mean - standard deviation

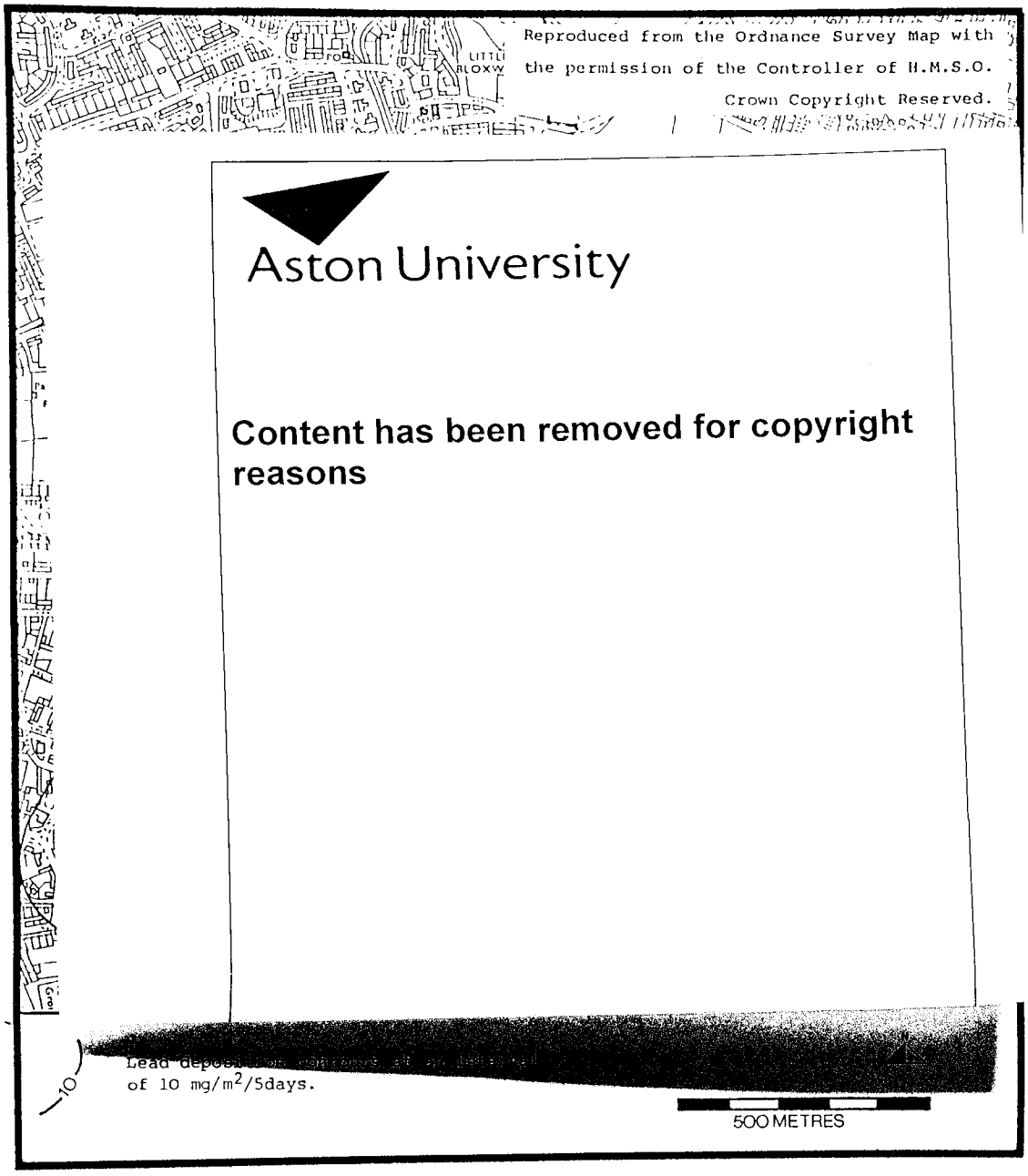


FIGURE 6.9 The distribution of lead fallout downwind of a secondary copper refinery measured using the snow surface technique reported in Appendix C.

deposition is confined to within 500 metres of the works boundary. This is illustrated by the deposition contours in Figure 6.9 which have been fitted to the results of the lead deposition measurements given in Appendix C. Figure 6.9 also highlights another feature of the results and that is the large spatial variability of deposition over short distances, even at the works boundary deposition is observed that is more typical of background levels. Clearly this is due to the wind direction during the sample period and the timing of source emissions (ie episodic or continuous) in relation to wind direction.

6.3.4 Implications of spatial variation for deposition measurement

The nature of the spatial variability of deposition controls the area representativeness of deposition measurements. The results of the analysis of spatial variance contained in Table 6.7 indicate that variations in deposition across an area of $1Km^2$ are sufficiently large to make a single measurement an unreliable estimate of deposition within this area. Indeed for lead the variation of deposition levels at the location scale are large enough to raise questions over the area representativeness of a single cannister. For example, in the fourteen groups of cannisters used to estimate location variance the location coefficient of variation in the absence of measurement error is 88.7% for lead compared to only 22.6% for cadmium. When the error involved in measuring deposition is taken into account the coefficient of variation for the location scale become 90.1% for lead and 40.9% for cadmium. To obtain reliable estimates of the mean deposition rate at a location a greater sampling density may be required for which the standard error of the sample mean would be given by $\sigma_L / \sqrt{n}$.

In previous surveys of urban deposition the practical difficulties associated with the operation of deposit gauges have meant that there have been only a small number of measurement sites to represent deposition in an entire urban area. The results of this spatial analysis would raise doubts over the area representativeness of these measurements and confirm that the conventional deposit gau ge is not an appropriate sampling instrument for examining the spatial distribution of deposition. The deposit cannister type of sampling instrument allows a large number of sample to be taken thus overcoming the problem of representativeness.

A possible explanation of these comparatively large spatial variations over distances less than $100m^2$ is that sample sites are located in the proximity to local sources in such a way that their observations could be sensitive to wind direction. If wind direction happens to coincide with the line joining a single sample site to source, but no others, then larger spatial variance could result. An alternative explanation could be that variation in micro- meteorological conditions (mainly windspeed) over the area of $100m^2$ differentially influences the efficiency of deposit cannister collection. Spatial variations occuring over a larger scale of upto $1Km^2$ probably represent a combination of random variation due to differences in deposition occurring as a result of localised sources within the area and general trends across grid squares resulting from the overall trends between one type of area and another.

6.4 Conclusions

6.4.1 Lead and cadmium deposition in Walsall

1) Lead and cadmium deposition in the Walsall study area have been shown to be log-normally distributed with a geometric mean lead deposition rate of 1.38 mg/m^2/30d and a geometric mean cadmium deposition rate of 0.05 mg/m/30d. The range in lead deposition covers four orders of magnitude from 0.03 - 51.4 mg/m^2/30d with 95% confidence interval of 1.22 - 1.56 mg/m^2/30d and the range of cadmium deposition covers two orders of magnitude from 0.01 - 0.64 mg/m^2/30days with a 95% confidence interval of 0.04 - 0.06 mg/m^2/30d.

2) The highest 1Km^2 area mean deposition rates for both metals occur in the central industrial area of Walsall and tend to decrease to the lowest values which are found in the non-urban and low density residential areas of the borough. There is some evidence to indicate that levels of both metals are affected by proximity to industrial activity; however this issue is explored in depth in Chapter seven and so is not pursued further here.

3) Average deposition is Walsall observed in this research appears to be in the range reported for other urban areas.

4) When compared with the deposition standards used in the F.D.R, 0.3% of sites exceed the maximum standard for long-term lead deposition compared to 4.0% of sites which exceed the maximum standard for long-term cadmium deposition. These results should be treated with some caution pending further investigations of the relative performance of the deposit cannister.

6.4.2 Spatial variation of lead and cadmium deposition

1) The results of spatial analysis are summarised in Table 6.7. These results show that single measurements of the type employed in previous deposition surveys only provide reliable estimates of deposition within a very limited area; for lead this area is less than $100m^2$. Even deposition levels within a $1Km^2$ area show considerable variation. This is assumed to be as a result of the heterogenous nature of the urban environment and the localised nature of source hotspots demonstrated by the 'snow study'. Thus detailed surveys of the spatial patterns of deposition in urban environments require a comparatively high sampling density, both of gauges per location and also locations per $1Km^2$ area. Such large sample densities are not possible using conventional deposit gauges and this reinforces the need for cheap and versatile sampling instruments such as the deposit cannister or the snow surface technique.

CHAPTER 7

IDENTIFYING SOURCES OF HEAVY METALS IN DEPOSITION

7.1 Introduction

7.1.1 Outline

The spatial pattern of deposition within an urban area such as Walsall will generally reflect the distribution of sources of metals to the atmosphere. The issue of spatial variability of deposition has been examined in detail in the preceding Chapter 6. This chapter aims, firstly, to identify the sources of heavy metals in deposition using the statistical methods of Factor Analysis and Cluster Analysis and then, secondly, to develop a deposition prediction model using the results of the Factor Analysis (Ob.3).

7.1.2 Summary of the Chapter

Section 7.2 details the application and the interpretation of the factor model which identifies sources of deposition on the basis of common variance between a number of heavy metals. Section 7.3 identifies spatial patterns of deposition arising from similar sources using the statistical technique of Cluster Analysis. Section 7.4 considers the development of the factor model to allow predictions of source derived deposition. The key findings of the chapter are summarised in section 7.5.

7.2 The development of a multivariate factor model for identifying sources of heavy metals in deposition

7.2.1 Introduction to the Factor model

This section describes how Factor Analysis (F.A.) can be applied to the data matrix to identify source processes which contribute to the observed spatial variance of deposition in Walsall.

For the purposes of applying a factor model the total variation in a set of multivariate observations is taken to consist of three component variances:

'spatial variance'

total variance = common factor variance + specific variance + error

unique variance

where common and specific variance represent 'real spatial variance' which is associated with causal mechanisms (source processes). Error variance is equivalent to analytical error discussed in chapter 5.

F.A. identifies groups of interrelated variables using information contained in the principal matrix of correlations between variables (ie. common factor variance). The objective of this technique is to replace the original variables by a smaller number of independent variables or 'factors'. These factors are taken to reflect specific source influences and can be used to construct source 'signature'

profiles. Figure 7.1 outlines how the F.A. method has been applied to identify sources of metals in deposition. The remainder of this section details these various analytical stages.

7.2.2 Application of factor analysis to Walsall deposition data

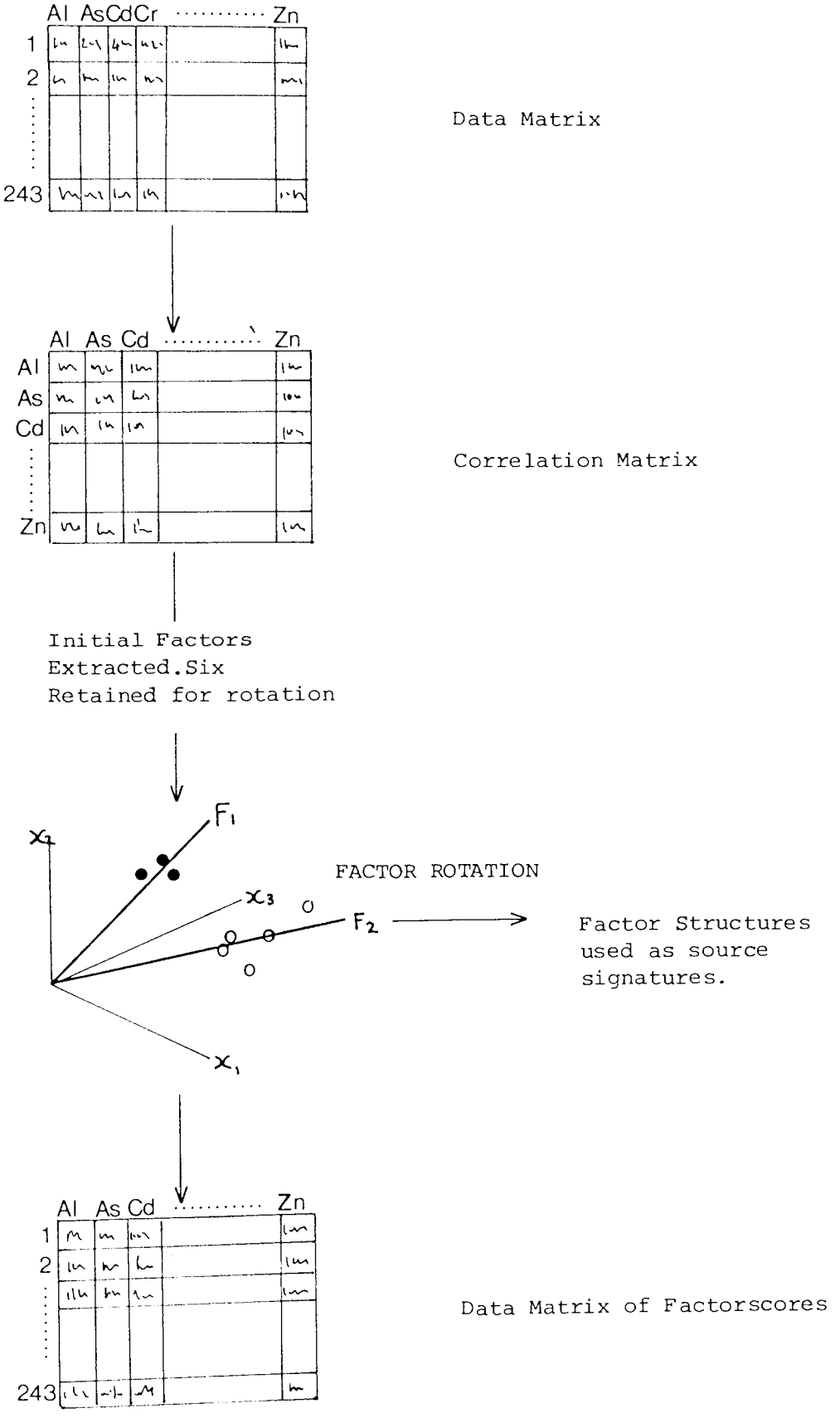
The first stage of F.A. involves computing the inter-elemental matrix of correlation coefficients. In this application the correlation matrix was computed from the results of survey 1 which had been specifically designed to provide measurements from a wide range of environments for the purposes of applying a factor analysis. This matrix is given in Appendix D from which it can be seen that most of the ten metals are significantly positively correlated. The factor model replaces the principal diagonal of this correlation matrix with estimates of a variable's communality[1]. In Principal Component Analysis (P.C.A.) the principal diagonal is taken as 1.0, thus giving defined factors. P.C.A. is therefore an orthogonal rotation of the original variable axes. As such it does not resolve the variation in the data set into underlying causalities. In F.A. however, the communality estimate produces factors which are inferred. F.A. is superior for identifying interrelationships (Johnston, 1978).

The next stage of the analysis is the orthogonal rotation of the correlation matrix. In this rotation the new axes (factors) are

---

1 This communality of a variable is the amount of variance that is accounted for by the common factors. If the factors account for the total variance then the communality is equal to 1.0. Kim (1975) discusses the technical details of communality estimation.

FIGURE 7.1 SCHEMATIC DIAGRAM OF THE SOURCE IDENTIFICATION PROCEDURE USING FACTOR ANALYSIS.



assumed to be independant. The resultant factor matrix usually produces as many factors as original variables. However, some of these are only marginal in terms of variance explained and are usually taken as factors representing experimental errors. Therefore, some of the minor factors are excluded from further analysis. Rummel (1970) and Harman (1967) both consider various criteria that can be employed to decide how many factors to retain. In this application six factors were retained as the maximum number of factors that were in themselves interpretable. The sixth factor has an eigen value[1] of greater than 0.5 indicating that it is of minor significance. Table 7.1 gives the variance explained by the ten factors derived from the initial rotation. From this table it can be seen that by retaining the first six factors 88.2% of the total variance is included in the factor model. These factors are assumed to evidence six kinds of source influence. The initial factor matrix is of limited interpretive value. However, further

Table 7.1 Variance estimates for the initial 10 factors

Factor	Eigen value	% of variance	Cumulative %
1	3.93	39.3	39.3
2	1.51	15.1	54.4
3	1.18	11.8	66.1
4	0.92	9.2	75.3
5	0.74	7.4	82.7
6	0.55	5.5	88.2
7	0.43	4.3	92.6
8	0.35	3.5	96.0
9	0.22	2.2	98.3
10	0.17	1.7	100.0

1 The eigen value is the sum of the squared factor loadings and indicates the total variance accounted for by a factor.

rotation of this matrix can highlight groups of interrelated variables. Various rotational methods are available, of these some preserve factor orthoganality while others allow factors to be correlated. In this particular application it is unrealistic to assume that sources are not to some degree spatially contiguous and therefore an oblique rotation was used in which factor orthogonality was relaxed. However, it should be noted that Hopke et al (1974) found that in the case of airborne particulate matter, rotational method did not greatly influence the interpretation of final factors.

The factor matrix produced by the oblique rotation for six factors is given in table 7.2. This is the Factor Structure Matrix which delineates the oblique simple structure interrelationships among variables. The factor profiles can be interpreted as source signature profiles. The factor loadings[1] define the separate clusters and indicate the degree of involvement of each variable on each factor profile. The percentage of common variance is a measure of the relative importance of each factor in contributing to the total common spatial variability of deposition in Walsall.

The factor correlation matrix given in table 7.3 indicates the orientation of factor axes. The coefficients may be interpreted as cosines of angles between axes. A non-zero coefficient indicates that data patterns are themselves correlated which in turn suggests spatial correlation between sources. In urban areas this would be

---

1 Factor structure loadings are the proportion of the variance in the variable associated with the variance in the factor.

expected due to the nature of the spatial distribution of sources. For example, industrial sources will tend to be located in industrial areas rather than rural areas.

Table 7.2 Factor structure matrix (oblique rotation solution)

	Factor loadings					
	F1	F2	F3	F4	F5	F6
Al	0.744	0.304	0.402	0.259	0.274	0.475
As	0.592	0.320	0.231	0.529	0.372	0.454
Cd	0.317	0.194	0.256	0.359	0.186	0.733
Cr	0.252	0.212	0.438	0.200	0.859	0.215
Cu	0.232	0.299	0.096	0.856	0.224	0.471
Fe	0.244	0.176	0.978	0.098	0.598	0.372
Pb	0.256	0.781	0.189	0.617	0.332	0.278
Mg	0.814	0.095	0.217	0.175	0.219	0.308
Mn	0.684	0.233	0.707	0.241	0.349	0.428
Zn	0.161	0.931	0.146	0.250	0.205	0.228
Variance	3.642	1.311	0.963	0.646	0.422	0.240
% of Variance	50.4	18.2	13.3	8.9	5.8	3.3

_____ large factor loading

Table 7.3 Factor correlation matrix

Factor correlations coefficients, r

	F1	F2	F3	F4	F5	F6
F1	1.000					
F2	0.199	1.000				
F3	0.321	0.167	1.000			
F4	0.265	0.358	0.079	1.000		
F5	0.260	0.244	0.455	0.258	1.000	
F6	0.414	0.240	0.342	0.441	0.239	1.000

(F1 ..... F6 = Factor/..... Factor 6)

7.2.3 Interpretation of factors

The six factors extracted from the original data matrix are taken as evidence of six types of source influence. Interpretation of these factors is made on the basis of the factor loadings given in the Factor Structure Matrix (table 7.2). Variables with large loadings are assumed to be components of a particular source signature. Variables with low loadings are assumed to be less important to the signature. The derived elemental profiles are then compared to the profiles that would be expected from various sources. As an example, if a factor was found to have high loadings on lead and bromine this could be taken as indication of a petrol combustion source (the Pb/Br ratio is often used as a simple form

of source tracer for vehicle emissions). The following are general interpretations of the six factors derived in the Factor Analysis:

(a) Factor 1

This factor appears to represent crustal sources in the Walsall area and is strongly dependent on deposition of aluminium and magnesium and moderately dependent on arsenic, cadmium and manganese. Two possible crustal sources could account for this factor; crustal weathering and coal combustion. Aluminium is frequently used as a marker for crustal sources and aluminium, magnesium and manganese are all major constituents of soil (Gaarenstroom, Perone and Moyers, 1977). The ratio of these elements in suspended particles arising from coal combustion relative to aluminium are similar to the ratio in crustal dust (Hopke et al, 1976). However, arsenic is associated with emissions from coal combustion (commission of the European Communities, 1980) and has been found to be elevated in the atmosphere due to this source (Salmon et al, 1977). The fact that arsenic is moderately loaded on this factor therefore suggests that this factor may represent coal combustion sources rather than crustal weathering. This is confirmed in section 7.3.2 following further examinations of this factor.

(b) Factor 2

The second factor is strongly loaded on lead and zinc and is attributed to vehicle and roadway sources. Lead is known to be associated with vehicle emissions from combustion of leaded petrol and tyres contain substantial concentrations of zinc typically

ranging from 8000 to 12000 ug/g in the rubber (Hopke et al, 1980). Linton et al (1977), in a study of urban roadway dust have attributed a factor loaded on both lead and zinc to traffic. Gatz (1978) attributes a similar factor to traffic sources and industrial metal sources.

(c) Factor 3

The third factor is attributed to iron foundry emissions. This factor has high loadings for iron and manganese and moderate loadings for aluminium and chromium. Both iron and manganese are major constituents of the larger sized particles emitted from iron foundry furnaces (Gatz, 1978). These sources are prominent in the Walsall area. In section 7.4 further investigation confirms that this factor is strongly associated with iron founding activity in the borough.

(d) Factor 4

The fourth factor is related to arsenic, cadmium, copper and lead and is interpreted as a secondary copper refinery factor. There are three large secondary copper refineries in the Walsall area which have been the subject of intensive scientific investigation. A recent survey of airborne contamination has demonstrated that all three works are significant sources of lead, copper and zinc to the atmosphere (Davis and Clayton, 1974). The investigation of deposition around one of the refineries described in appendix C has shown this to be a prominent source of both lead and copper fallout.

(e) Factor 5

The fifth factor is heavily loaded on chromium and iron with moderate loadings on arsenic, lead and manganese. This factor was provisionally interpreted as a general grouping of metallurgical sources on a single factor. Iron and manganese suggest that the iron and steel industry is linked with the factor. The dependence on chromium could be a reflection of the chromium plating industry and also a ferrochrome manufacturing facility in the Walsall area. Arsenic suggests coal combustion which could be a reflection of coke used in metallurgical furnaces such as cupolas.

(f) Factor 6

The final factor is only marginal in terms of the variance explained but was included in the analysis because of its strong association with cadmium. This factor is also moderately associated with aluminium arsenic, copper and manganese. The factor is interpreted as a composite factor reflecting the secondary copper refinery industry and coal combustian. Arsenic and copper are associated with copper refining. This factor is also correlated with the other copper refinery factor, factor 4 as indicated in the factor correlation matrix, table 7.3. Aluminium and manganese and arsenic are important elements of factor 1 - the coal combustion factor, again factor 6 is positively correlated with factor 1. Therefore, this appears to be a composite factor representing both source types.

These six factors and their hypothesised sources form the basis of the Factor Model as a source identification tool. The resolution

of this factor model is limited by the relatively small number of variables included in the analysis. Of course it should be stressed that factors only represent source processes causing variation in the data, ie. sources which are spatially ubiquitous and are associated with constant background deposition will not be detected through the factor model. Sources which are spatially intercorrelated will also cause difficulties for the factor model as they will tend to be represented on the same factor. If more elements could be included clearer separation of such sources could be achieved. Additional elements should be chosen as markers of specific sources, e.g. scandium for soil and dust, vanadium for fuel oil combustion, bromine for vehicle exhausts etc. Such additional analysis would require sophisticated analytical procedures. Neutron Activation Analysis or Inductively Coupled Plasma Spectrophotometry are examples of detection methods that could be extremely valuable for multi-elemental analysis as these allow a large number of elements to be determined in a small sample volume.

7.2.4 Measurement of factors using factorscores

The factor model produces a reduced number of newly created synthetic variables, factors. These variables can be measured using factor-scores derived for each of the original observations. With the factor model these factorscores can only be estimated. This is because factor analysis deals only with common variance, whereas the observed values of the original variables combined both common and unique elements in unknown proportions. Factorscores are therefore estimated by regressing the original data matrix on the loadings matrix (structure matrix), assuming that the average

proportions for the variance distribution are the same for each observation (Harman, 1967).

The importance of these factorscores stems from their interpretive value. Scores derived for every observation allow the geographic distribution of source factors to be examined in detail. The use of these factorscores to build a second receptor model based on cluster analysis is considered in the following section 7.3 and as a basis of a source model in section 7.4.

The factor profiles produced by the factor model yield no information on the actual levels of metals associated with each source. Therefore, the calculated factorscores provide only a relative measure of the importance of each source to each sample rather than determining the amounts of material deposited from various sources. One way in which quantitative estimates of source impact could be obtained is by using 'Q-type' Factor Analysis where the correlation between samples is examined rather than correlation between variables. This allows an analysis similar to that of the Chemical Elemental Balance where source profiles are used to solve a mass balance equation, but without the requirement of a 'a priori' knowledge of the number and nature of sources. This type of analysis has been successfully applied to source identification for suspended particulates (Alpert and Hopke, 1980, and Alpert and Hopke, 1981) and Hopke, Lamb and Natusch (1980) have had limited success using this technique to identify sources in road dusts. This type of analysis could in theory be applied to data on deposition if the rate of total mass deposition was readily available and the rate of deposition of bulk matrix components was known. This therefore represents one area of possible future development.

7.3 Multivariate receptor model based on Cluster Analysis

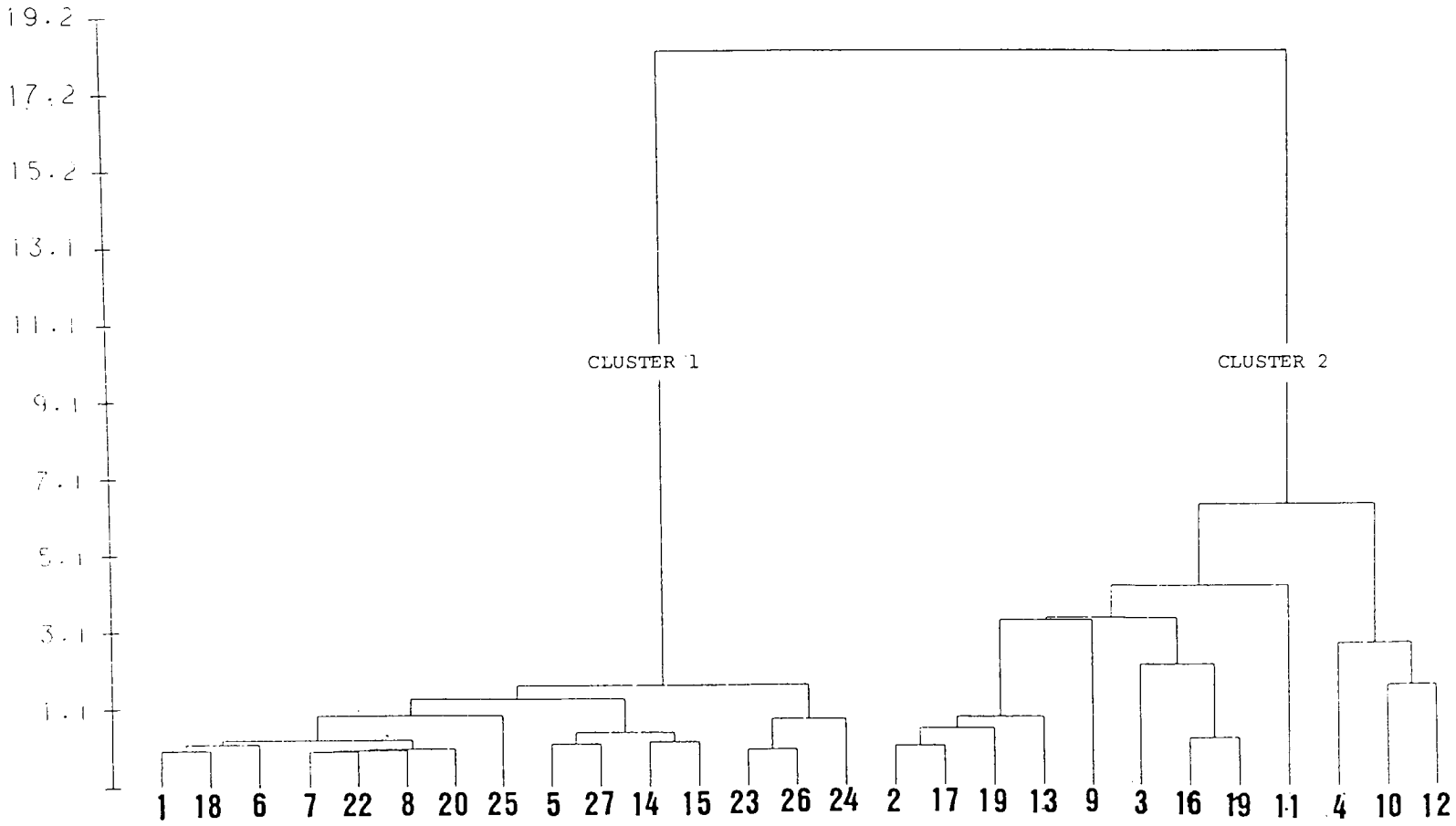
7.3.1 Geographic associations in deposition as an aid to source identification

The multivariate factor model developed in the previous section has identified sources from the inter-relationships between variables measured in the deposition survey. This type of receptor model makes no direct use of an important aspect of the information contained within the data, namely the geographic distribution of deposition. This section explores a second type of multivariate receptor model which is used to investigate spatial interactions in deposition. The method was based on the statistical technique of Cluster Analysis. Rather than isolating relationships between variables, Cluster Analysis aims to isolate groups or clusters of similar observations which can then be related to the geographic location of known source types. Clustering of points can be made against a range of criteria which are detailed by Everitt (1974). In this research minimum increase in error sum of squares was taken as the criterion for building clusters using the hierarchical method known as Wards' method (Ward, 1963). The analysis was performed using the Clustan 1B statistical package (Wishart, 1982) on the University of Aston, Harris computer system.

7.3.2 Application of Cluster Analysis

A number of cluster models have been used to analyse the spatial associations between different areas of Walsall. Three of these have proved valuable in understanding the nature of the spatial

FIGURE 7.2 DENDROGRAM SHOWING THE RESULTS OF THE CLUSTER ANALYSIS OF SAMPLE SQUARE DEPOSITION.



Grid square codes (for location see Figure 4.4).

distribution of deposition. These are based on:

- clustering of grid square means,
- clustering of site deposition levels,
- clustering of factorscores.

The first cluster model was developed from $1km^2$ sample square mean deposition rates in order to examine the more general relationships in deposition throughout Walsall. The results of this model are represented as a 'dendrogram'[1] in figure 7.2 in which two main clusters are apparent. To assist in the understanding of what these two clusters represent, average values for each cluster for all ten variables have been calculated. These average concentrations are given in table 7.4. When cluster members are traced to the sample square location map (figure 4.4), these two clusters are seen to represent a grouping of all residential/rural sample squares in cluster 1 and industrial/urban squares in cluster 2. The mean deposition levels in cluster 2 are greater than those of cluster 1: in most cases by a factor of about 2. This cluster model is useful as it confirms that at a very general level urban/industrial areas experience higher metal deposition levels than rural/residential areas. Clearly this reflects the nature of the sources that are located in urban/industrial areas.

---

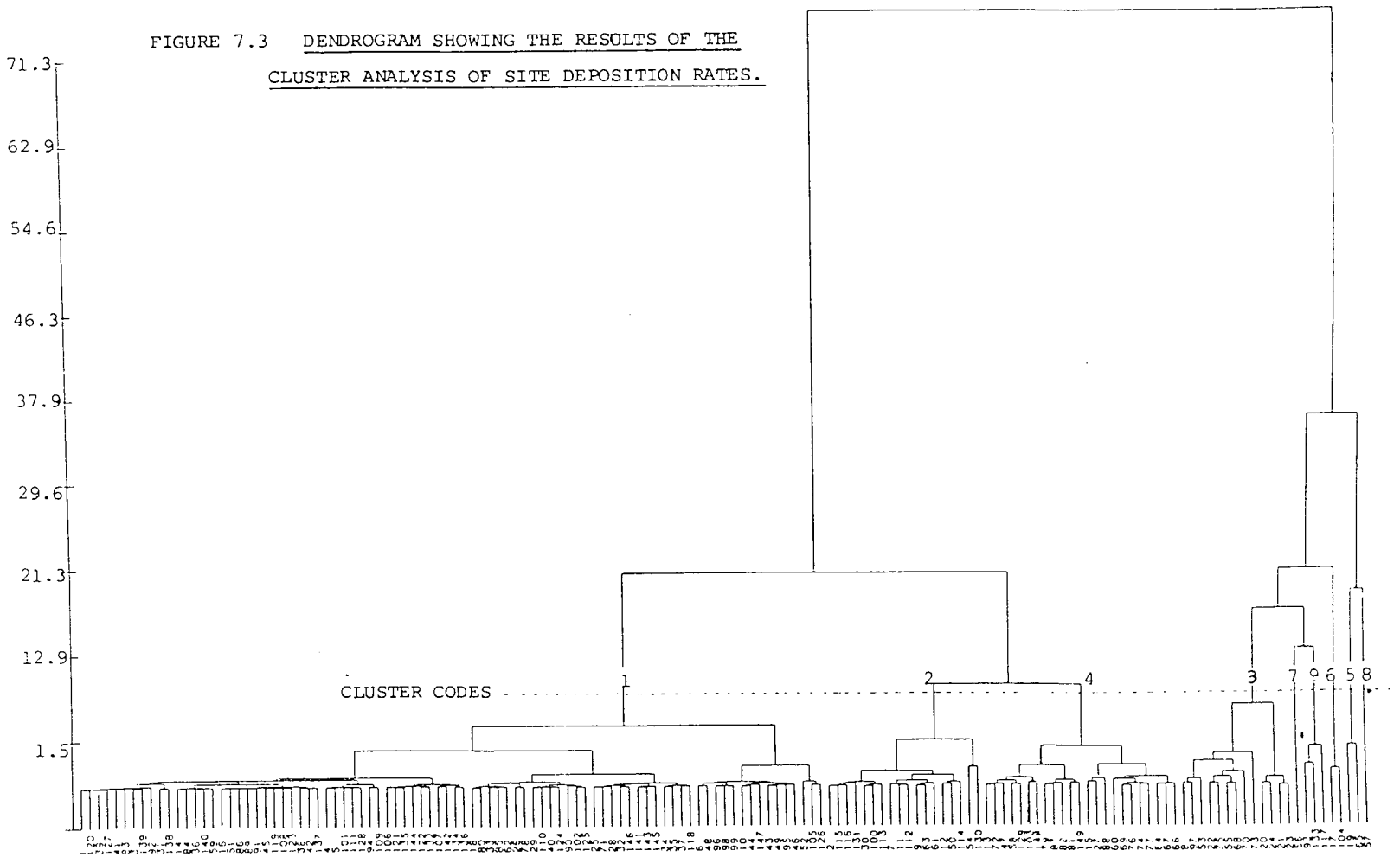
1 A dendrogram is a cluster diagram which helps to indicate the relationships between individual samples. The dendrogram is interpreted by examining the way in which the samples group together to form clusters and the way in which the clusters combine.

Table 7.4 Cluster means and standard deviations for the two main sample square clusters ($mg/m^2/30d$)

	Cluster 1		Cluster 2	
	Mean	Standard deviation	Mean	Standard deviation
Al	6.7	1.26	13.5	3.4
As	0.027	0.007	0.040	0.012
Cd	0.05	0.03	0.07	0.04
Cr	0.14	0.05	0.36	0.24
Cu	1.26	0.92	6.82	7.62
Fe	14.3	5.4	33.1	13.6
Pb	1.26	0.69	3.40	2.35
Mg	4.79	1.59	8.39	4.40
Mn	0.71	0.47	1.79	0.63
Zn	32.9	14.4	50.7	23.6

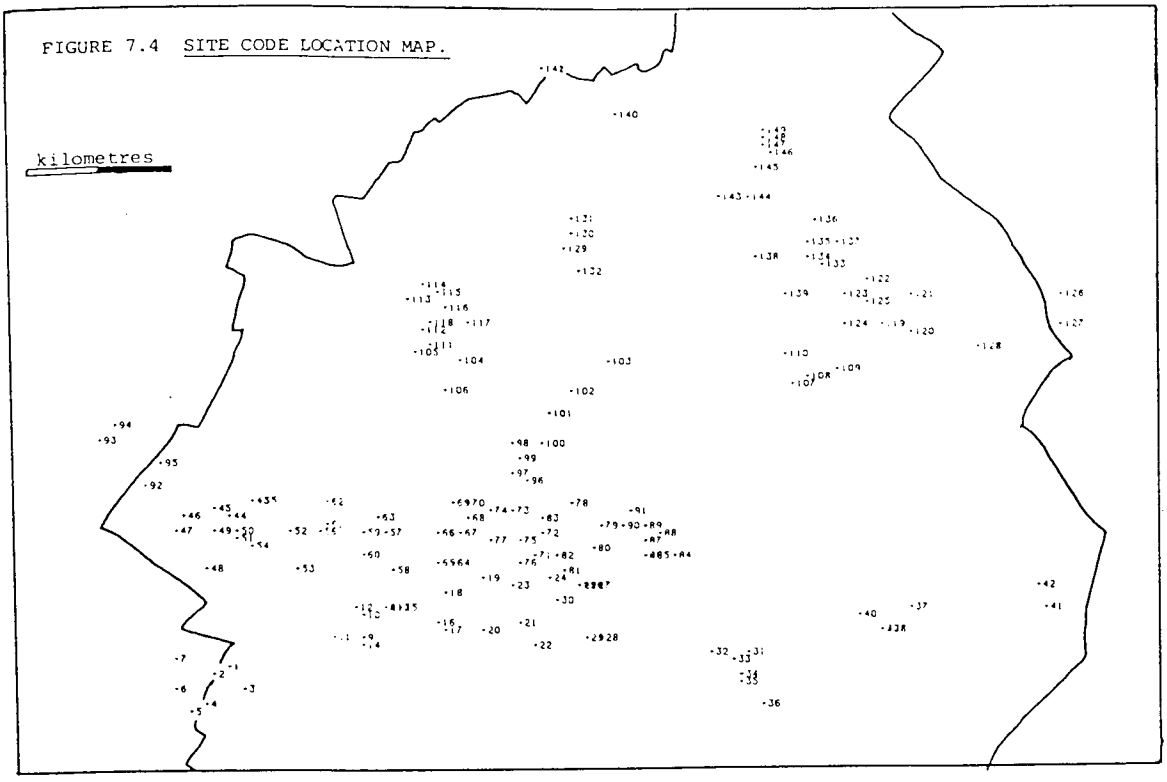
The second cluster model is based on site deposition levels rather than grid square means and is used to identify sites with similar deposition rates. Only sites with no missing observations were included in the analysis. Nine clusters were identified. The dendrogram for these nine clusters is given in figure 7.3 where the site code numbers refer to the site code location map given in figure 7.4. In figure 7.5 the clusters have been mapped onto the Walsall base map to illustrate how the cluster groups are distributed. Cluster 1 is seen to contain sites largely located in rural or low density residential areas. Cluster 2 - 9 are all located either in urban areas or/and in the vicinity of industrial sources, for

FIGURE 7.3 DENDROGRAM SHOWING THE RESULTS OF THE CLUSTER ANALYSIS OF SITE DEPOSITION RATES.



Site reference codes (see Figure 7.4).

FIGURE 7.4 SITE CODE LOCATION MAP.



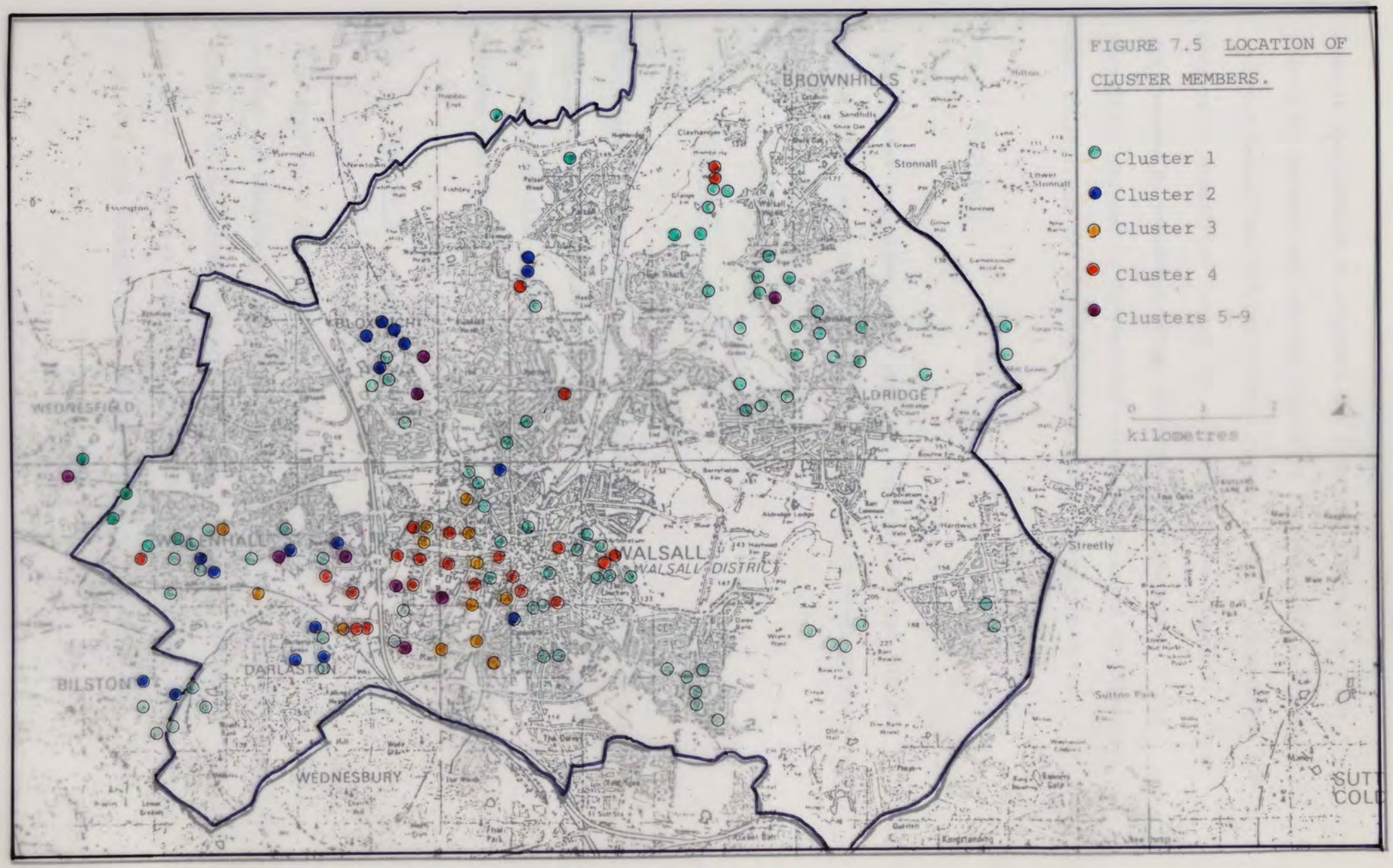


FIGURE 7.5 LOCATION OF CLUSTER MEMBERS.
Cluster 1
Cluster 2
Cluster 3
Cluster 4
Clusters 5-9
kilometres
BROWNHILLS
Stonnall
ALDRIDGE
WEDNESFIELD
WALSALL
WALSALL DISTRICT
Streetly
DARLASTON
BILSTON
WEDNESBURY

example the members of clusters 5 - 9 are all located next to industrial sources and can be considered as representing hotspots of metal deposition for one or more metals. Table 7.5 contains the mean metal deposition levels for each of the nine clusters. These are assumed to represent sites where similar influences affect deposition and can be interpreted using the location of sites in each cluster and the average cluster metal deposition rates.

(a) Cluster 1

This cluster comprises sites with low deposition rates for all metals which tend to be located in rural and low density residential areas of the Borough.

(b) Cluster 2

This cluster contains those sites located in urban areas which have high zinc deposition levels. The majority of sites are sited near to industrial zinc sources. For example, sites 112 - 116 are all located near to the Zinc Alloy works at Bloxwich.

(c) Cluster 3

This cluster is characterised by sites with high copper, iron, lead, cadmium and manganese deposition rates. The sites in cluster 3 are located in the Walsall/Pleck area where there are a number of potential industrial metal sources, including the copper refinery at Pleck, iron foundries and numerous small metal works.

TABLE 7.5 Mean metal deposition rates for nine clusters.

Element	Clusters 1	2	3	4	5	6	7	8	9
Aluminium	7.51	10.86	25.12	12.01	12.65	16.10	22.90	25.10	22.20
Arsenic	0.026	0.030	0.048	0.055	0.052	0.079	0.040	0.073	0.043
Cadmium	0.044	0.084	0.092	0.089	0.075	0.210	0.640	0.100	0.080
Chromium	0.14	0.21	0.44	0.29	2.98	0.55	0.31	0.48	0.57
Copper	1.42	3.88	5.41	4.68	4.05	54.34	4.18	9.17	2.31
Iron	16.63	22.54	42.91	18.56	110.55	26.30	104.30	40.00	131.50
Lead	1.20	2.53	3.29	2.65	8.91	18.47	1.64	51.43	4.45
Magnesium	4.64	6.31	16.67	9.22	8.45	10.20	10.90	10.50	9.93
Manganese	0.69	1.03	3.06	1.65	2.68	3.73	4.47	3.28	9.96
Zinc	26.77	95.33	27.50	37.30	72.90	85.90	40.20	389.50	88.47
Number of sites	86	18	13	23	2	2	1	1	3

(d) Cluster 4

Cluster 4 contains sites with high cadmium, copper, lead and zinc deposition. These sites are predominantly located in the central urban area between Walsall and Willenhall. Again there are numerous sources in this area.

(e) Clusters 5 - 9

As stated previously sites in these clusters are elevated in one or more metals and tend to be located close to identifiable industrial sources. These include iron foundries (sites 19, 93, 104, 117 and 113), copper refineries (sites 17, 56 and 65) and a scrap yard near to the M6 motorway (site 57).

These cluster groupings are useful as they confirm that certain areas of Walsall are characterised by deposition that can be associated with certain types of source, predominantly metal industries. However, certain of these groupings can be explained by a number of potential source processes, particularly clusters 3 and 4.

To overcome the problem of interpreting clusters where the source or sources are not readily identifiable, and also to assist in the interpretation of the factor analysis a third form of Cluster Analysis was used. This was based on clustering factorscores. The results of this analysis produce a similar classification of sites to that resulting from the analysis based on metal deposition rates. The average factorscores for each cluster are given in table 7.6. Clusters 5 - 9 have been collapsed into two clusters 5 and 6. The

TABLE 7.6 Cluster mean factor deposition rates for six clusters.

Factors	Clusters					
	1	2	3	4	5	6
1	-1.38	-0.04	2.23	1.84	4.81	6.86
2	-0.16	-0.05	1.61	-0.27	2.14	-5.59
3	-0.25	-0.08	1.03	0.68	0.87	-1.93
4	0.08	-0.31	-0.68	0.71	0.62	0.58
5	0.00	0.13	-0.50	-0.09	0.60	-0.66
6	0.07	-0.08	-0.11	-0.30	1.76	1.42
Number of sites	73	40	13	14	6	3

factorscores are in standardised cluster form so that the mean value is zero; below average values are indicated by negative cluster means, and above average values by positive cluster means. These cluster averages can be used to refine the interpretation of factors and also to identify sources in areas where the analysis of metal deposition levels was inconclusive.

(a) Factor 1 - Coal combustion factor

Clusters 1 and 2 have low Factor 1 deposition rates. Sites in these clusters are located in rural areas or in areas of low density housing and smoke control zones. Sites in clusters 3 and 4 have above average Factor 1 deposition. These tend to be located in the older urban areas around Walsall and Willenhall where the housing is generally high density council estates or Victorian terraces not yet covered by smoke control orders.

(b) Factor 2 - Roadway/vehicle sources

Cluster 1 and 4 have below average Factor 2 deposition. Cluster 1 contains sites in rural areas where the road network density is low. Cluster 4 comprises sites in the older areas of Walsall, typically sites near to minor roads or on industrial estates where traffic volume is comparatively low. Cluster 2 has average Factor 2 deposition and this contains sites mainly located in medium road network density areas such as interwar council housing estates. Cluster 3 has above average deposition for this factor. Sites in cluster 3 are predominantly located in industrial/commercial areas of Walsall, Caldmore and Birchills. Such areas would be expected to have high levels of traffic related pollution.

(c) Factor 3 - Ironfoundry sources

Sites with above average deposition of this factor (clusters 3, 4 and 5) tend to be from areas associated with ironfounding activity: mainly Walsall, Bloxwich and Willenhall. Sites with below average deposition of Factor 3 (clusters 1 and 2) are generally from rural/residential areas of urban areas not connected with ironfounding, e.g. Darlaston.

(d) Factor 4 - Copper refinery sources

Above average deposition of this factor occurs in clusters 4, 5, and 6. These are predominantly located in the Walsall/Pleck area within two kilometres of the large copper refinery at Pleck. Two sites from cluster 4 are located next to secondary copper refineries in other parts of the Borough.

(e) Factor 5 - Metallurgical Processes

This factor was provisionally interpreted as a general metallurgical factor possibly representing ironfounding, chrome plating and/or coal combustion. Clusters 2 and 5 have above average deposition on this factor. Sites in these clusters are located in urban areas but they are not linked to identifiable sources except for some sites in cluster 2 which are located near to a chrome plating works at Birchills. This disparate collection of sites does not provide additional insight into the nature of this factor other than its association with urban areas.

(f) Factor 6 - Copper refining and coal combustion

Cluster 5 and 6 have high rates of deposition of this factor. Sites in Cluster 6 are all located within one kilometre of the copper refinery at Pleck. Sites in cluster 5 are located in ironfoundry areas. Ironfoundries rely on coking coal as an energy source and this may explain the connection with coal combustion. However, this factor is only marginal in terms of variance explained and as such may also represent error variance associated with the elements loaded on this factor. Therefore these interpretations should be treated with some caution.

This analysis demonstrates how the combination of Factor and Cluster Analysis can be used to identify source processes for heavy metals in deposition. Joint application is of greater value than either technique used in isolation because source identity is based on source signature profiles and geographic distribution of factors in relation to their hypothesised sources.

7.3.3 General conclusions in respect of source identification

It is now possible to draw general conclusions regarding the sources of lead and cadmium in deposition in the Walsall area, in particular in the Walsall/Pleck area which has been observed to have generally elevated levels of both metals (section 6.2).

Lead deposition is strongly related to Factor 2 - the roadway/vehicle factor. This factor is prominent in the Walsall/Caldmore/Birchills area of Walsall. Lead is also associated with deposition of factor

4 - the copper refining factor. This is important in the Walsall/Pleck area. Thus it may be concluded that both roadway/vehicle sources and copper refining are strongly linked to the variance of lead deposition rates in the central Walsall area.

Cadmium deposition is moderately associated with Factor 1 - coal combustion and factor 4 - copper refining. These are prominent in the Walsall/Pleck/Willenhall area. The largest loading for cadmium however is for factor 6 which is tentatively ascribed to copper refining and coal combustion in the ironfounding industry. This factor is also associated with the Pleck area of the Borough. Therefore, the variance in cadmium deposition in the Walsall/ Pleck/Willenhall area can be largely explained by a combination of coal combustion, copperrefining and ironfounding activity.

An important aspect of the two methods that have been explored for the purposes of source identification is that they rely on associations between elements and sources and as such the source identity is inferred on the basis of hypotheses linking groups of metals to the sources' propensity to emit those metals. In the following section this linkage is tested using a source-based model applied to factor 3 and the ironfoundry industry.

An additional point to note is that these conclusions relate only to conditions in Walsall at the time of sampling. In the following section a method for generalising these results is explored in the case study of the ironfounding factor 3. This factor is taken because it is associated with a source that is important in terms of the amount of variance it explains (13.3% of common variance)

and for which it is comparatively straight forward to compile an emission inventory. Factors 1 and 2 both represent sources for which emission inventories would be less straightforward.

7.4 Source-based factorscore deposition model

7.4.1 Ironfoundry deposition

This section describes the development of a simple empirical model which has been calibrated against estimated emissions and deposition arising from the ironfoundry industry in Walsall. To overcome the traditional difficulties associated with calibrating and applying prediction models to emissions in complex multisource areas, the model is designed to predict deposition using factorscores as the dependent variable, as opposed to metal deposition rates. Therefore, this model is specifically designed to predict the relative source impact as opposed to absolute deposition rate of a particular heavy metal.

In section 7.2, factor 3 was hypothesised to relate to ironfoundry emissions. This factor is taken as the basis for the exercise in hypothesis validation. However, it may be possible to use the technique described here to model the deposition of emissions derived from other sources.

If the hypothesised interpretation of factor 3 is correct, then in principle the observed factorscore deposition could be reproduced through a mathematical model that predicts how emissions from ironfoundries are dispersed. In section 2.4 deposition in the vicinity of sources was noted to follow a simple distance - decline relationship. This relationship is used as the basis of the model.

7.4.2 Empirical calibration of a distance-decline model for factor 3 deposition

In section 2.4, it was noted that the most simple mathematical form of the 'distance-decline' approximates to an exponential decay. The process of gravitational setting of larger dust particles close to the source, followed by the setting/impaction of progressively finer particles at greater distances downwind of their source, (selective depletion) can be represented by the following theoretical mathematical model:

$$y = ax^{-b}$$

where y is the deposition rate at distance x from the source and a and b are analytical constants. However, the precise form of the decay curve may in practice be collected by both factors associated with the emission itself (eg. particle size distribution, aerodynamic properties, emission height, temperature and efflux velocity etc.) and factors which govern the diffusion/deposition process (eg. meteorological parameters, local obstructions to wind flow, surface roughness etc). As such, the simple negative exponential model forms an 'idealised' representation of the distance decline relationship.

This research has calibrated an empirical distance-decline model which assumes that ironfoundry-derived deposition can be described by a form of the exponential decay curve which takes into account specific factors which may affect ironfoundry deposition (eg. low emission height, comparatively large particle sizes etc). The form of the decay function taken as the basis of this empirical model was:

$$y = c - ax^b$$

where a, b and c are constants[1] determined from an empirical calibration procedure. The calibration procedure involved the use of a computer based model which was applied to an emission inventory of ironfoundry emissions in Walsall. The inventory was based on annual metal production estimates for each of the ironfoundries in the Walsall study area. The basic production data was obtained from a telephone survey of the ironfoundries concerned. The mass emission rate estimates were obtained by applying an emission factor and the emission estimating procedure is described in detail in Appendix A. As the model was based on data on deposition obtained over a period of 30 days it was necessary to take account of the variability in wind-directions and windspeeds (deposition would only affect monitoring sites during the proportion of the 30 day period when they were downwind of a foundry). To do this wind direction frequencies f_i were obtained for the eight major compass sectors (i = 1 to 8) for the relevant period of time. A site was assumed to be affected by deposition from a given foundry only for the proportion of time that the wind was blowing from the compass sector containing the foundry. The pattern of dispersion of deposition is affected by windspeed and therefore the mean directional wind velocities U were computed for each wind sector. This information is given in Table 7.7 which shows that the predominant

---

1 This type of exponential function was taken as the basis of the calibrated model for the technical computational reason that deposition at distance zero was to be computed. Whereas negative exponential model is asymptolic to the y axis and as such produces unrealistic values of deposition close to the source (infinity at zero distance).

wind direction was from the south to south west and that windspeeds were generally higher in the west than in the east.

The model was calibrated against the observed factor 3 factor sources using the general algorithm

$$y = \sum_{i=1}^{8} f_i \left[\sum_j \frac{Q_j}{\bar{u}_i} \left(c - a x_j^b \right) \right]$$

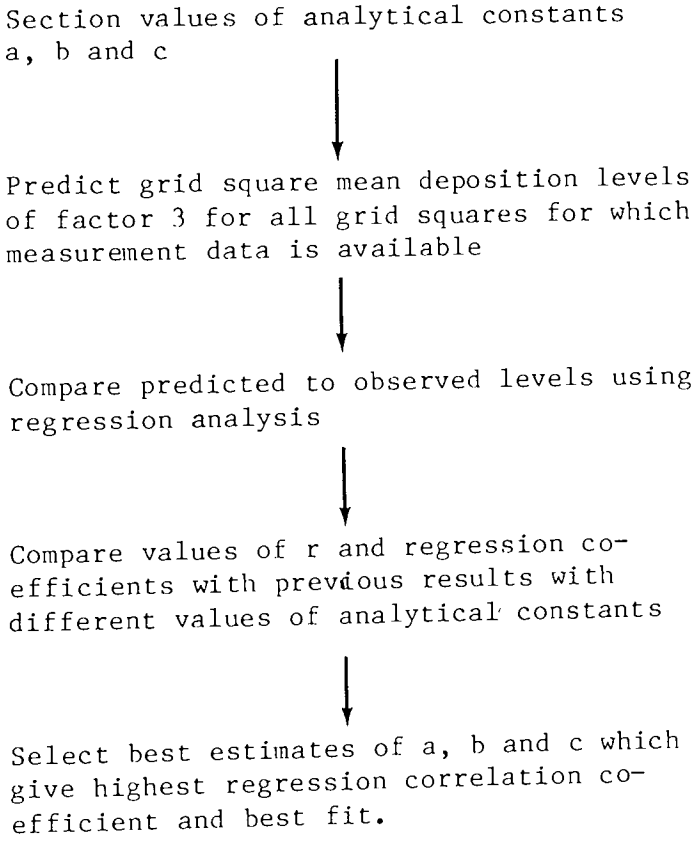
where y is the sum of deposition derived from i separate ironfoundries, f_i and $\bar{u}i$ are the frequency and windspeed of winds from the direction of foundry j, Q_i is the total mass emission rate of foundry i, and xj is the distance between the foundry j and the site at which deposition is estimated.

Table 7.7 Meteorological data for the sample period Nov - Dec, 1982

	f	$\bar{u}$ (m.p.h)
North	4%	8.3
North-East	4%	3.7
East	6%	4.0
South-East	5%	6.9
South	11%	17.6
South-West	27%	17.1
West	30%	15.9
North-West	13%	10.5
	100%	13.8

This model was applied using the Fortran 66 computer program listed in Appendix E. The procedure that was used to calibrate the model is summarised in Figure 7.6. Values of a, b and c were progressively modified in an iterative procedure designed to produce the best observed/predicted fit. At each stage the predicted 1km grid square factor 3 deposition rates were compared to the observed rates using least squares linear regression and the correlation coefficient, r[1]. The best model fit was produced using a = 0.347, b = 0.05 and c = 0.375. The correlation coefficient r, for the predicted to observed regression with these values was 0.843 indicating that 71.3% of the variance of factor 3 could be reproduced by the distance-decline model. The

Figure 7.6 Summary of the empirical calibration procedure



1 Grid square mean factor 3 deposition was computed as the arithmetic average of 25 points on a 5 x 5 grid within the square.

relationship between the predicted/observed factorscores is illustrated in figure 7.7[1].

The simple factor 3 deposition model can successfully reproduce 71.3% of the variance of factor 3. Thus 28.7% of the total variance is unexplained by the model. This represents prediction error and may reflect four potential sources of error in the model:

- inaccuracies in the emission inventory, particularly for foundries outside the borough area which may affect deposition in Walsall
- random variations in composition of emissions between different foundries and at the same foundry over time
- the episodic nature of emissions which may occur inequally during different wind directions
- unidentified sources may have an influence in factor 3.

The distance-decline model, when applied in this fashion, provides evidence to substantiate the hypothesis that factor 3 reflects deposition of ironfoundry-derived particles which are characterised by high concentrations of iron and manganese. It is possible that other factors could be used as variables in modelling exercises similar to this. However, this was beyond the limitations of this research and would require detailed information on the emissions from the sources they are hypothesised to reflect. Despite the general simplicity of the distance-decline model used in this

---

1 Note that the 'calibrated' estimates are compared with the same estimates used for determining the calibration coefficients, not with independant data.

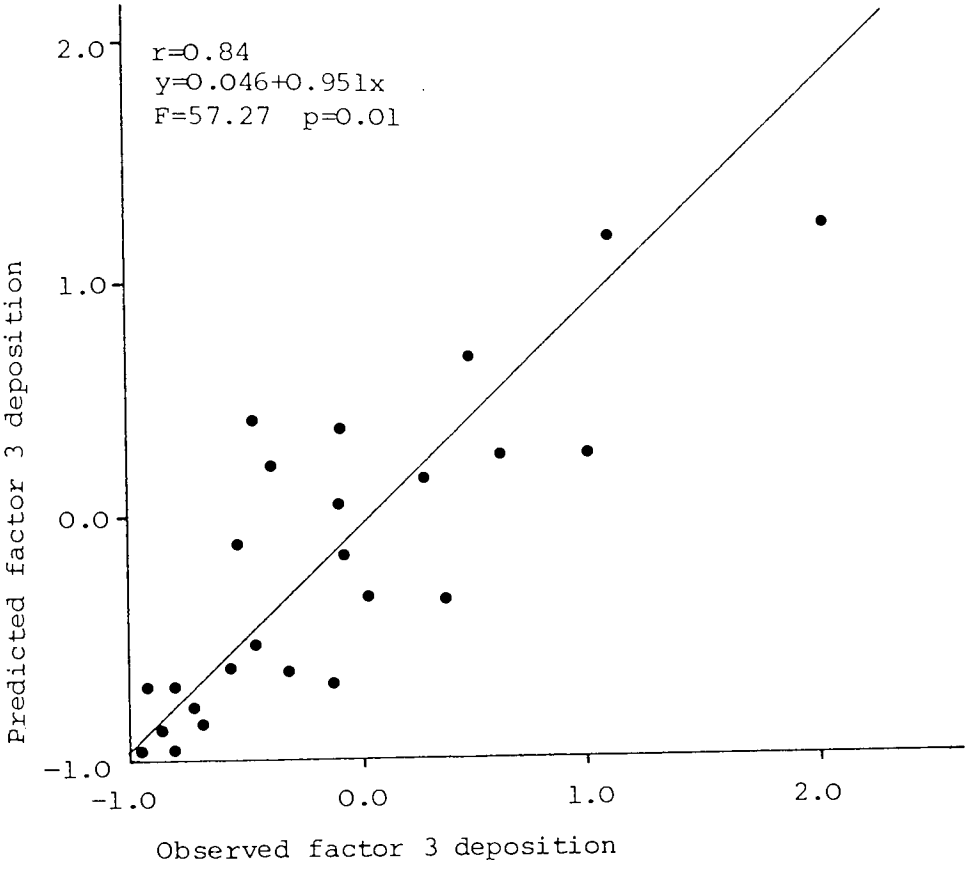


FIGURE 7.7 PREDICTED AGAINST OBSERVED FACTOR 3 DEPOSITION.

development application, the accuracy obtained in predicting ironfoundry deposition is comparable to predictions made by more sophisticated pollution diffusion models. For example Vanderborght et al (1983) have used a Gaussian dispersion model with source depletion to predict deposition arising from a single metallurgical works. Yearly average antimony deposition was predicted with an accuracy of 60%. In the field of air pollution modelling Turner, Zimmerman and Busse (1972) have evaluated a range of dispersion models for sulphur dioxide and particulates in New York. The sophisticated Air Quality Display model explained 79% of variance of SO_2 but only 39% of variance for particulates. The simple Gifford and Hanna area proportionality model (Gifford and Hanna, 1971), explained 66% of the variance of SO_2 and 40% of the variance of particulates.

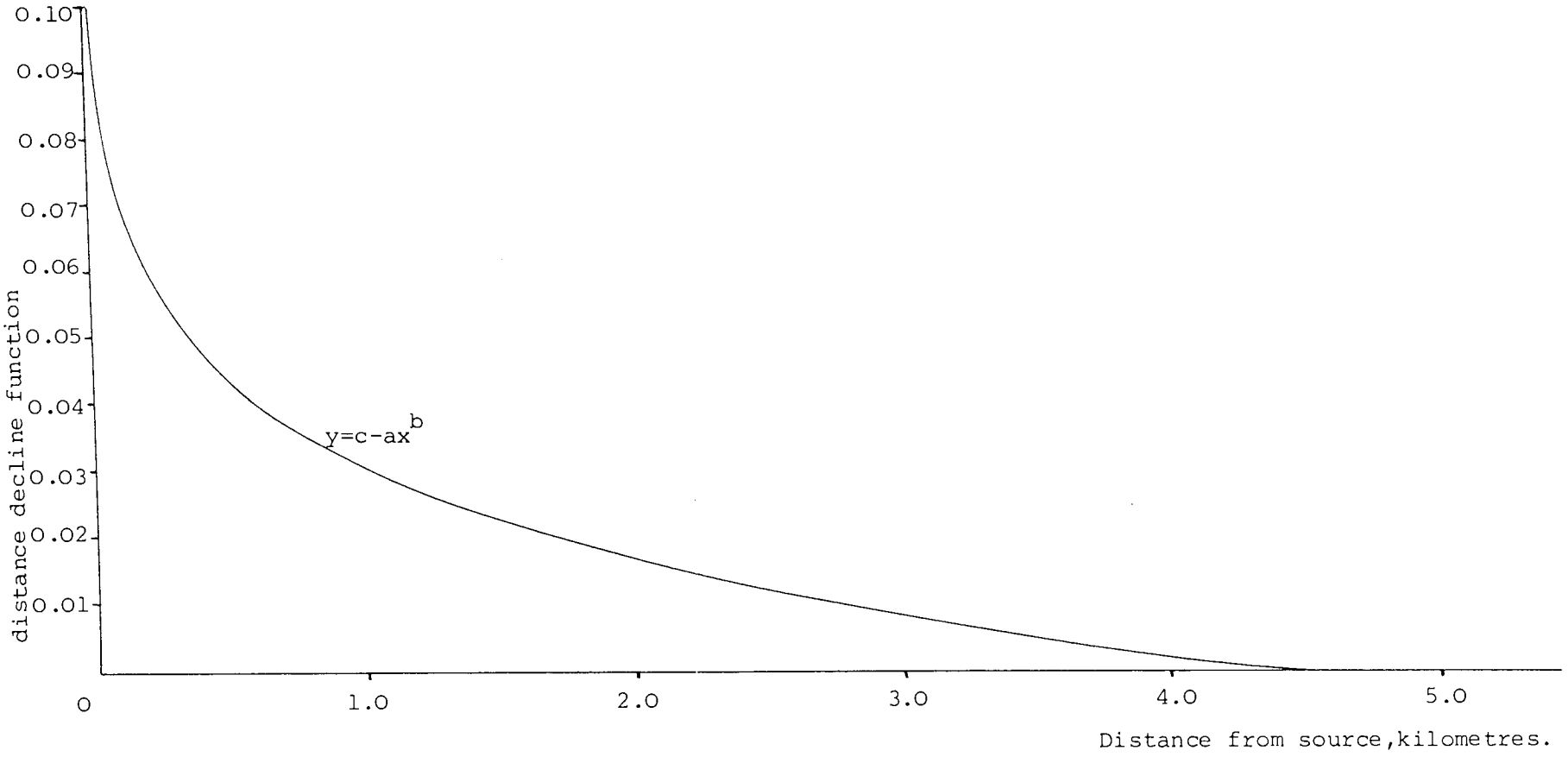
7.4.3 The spatial distribution of ironfoundry deposition

In addition to its hypothesis testing function, the model derived in the previous section may also be used to illustrate the spatial patterns of ironfoundry deposition. The distance-decline function has been plotted in figure 7.8 to illustrate the downwind decay pattern of deposition from ironfoundries. The combined effects of dispersion and depletion of airborne particle concentration produce a decreasing rate of deposition which reaches zero at a distance of between 4 and 5 kilometres. This rapid decay in deposition is indicative of large particle deposition by gravitational settling (ironfoundries are sources of large particles owing to the generally poor efficiency of pollution control devices employed in the industry). This issue is considered in Appendix A.

The calibrated distance-decline model can also be used to predict the relative impact of ironfoundry derived deposition over the whole of Walsall. In figure 7.9 the predicted deposition levels over the Walsall area for Nov - Dec 1982 are represented as a 'contour map' of factor 3 deposition. The contours, or isolines, are produced by a spatial averaging routine (GINOF-SURF). The same information is represented in figure 7.10 as a three dimensional map or isometric projection. These two figures clearly show that ironfoundry derived deposition reaches a maximum over the Walsall town centre area and generally declines away towards the rural areas.

The general elevation of ironfoundry deposition around Walsall/Bloxwich/Willenhall coincides with distribution of the majority of Walsall's cupola furances. The location of all of the ironfoundries that were operating in Walsall during the study is shown in figure 7.11. The impact of two cupola furnaces in the rural areas of Brownhills/Aldridge is clearly shown. However, the spatial pattern of deposition around these smaller foundries has not been adequately illustrated at the resolution used by the grid mapping procedure. The spatial distribution of predicted deposition in general reflects the location of foundries and the wind direction of frequency. This is illustrated by the rapid decline in deposition to the south of Walsall where there are no foundries and northerly winds were comparatively infrequent.

FIGURE 7.8 DISTANCE-DECLINE IN IRONFOUNDRY DEPOSITION DESCRIBED BY THE MULTIPLIER FUNCTION.



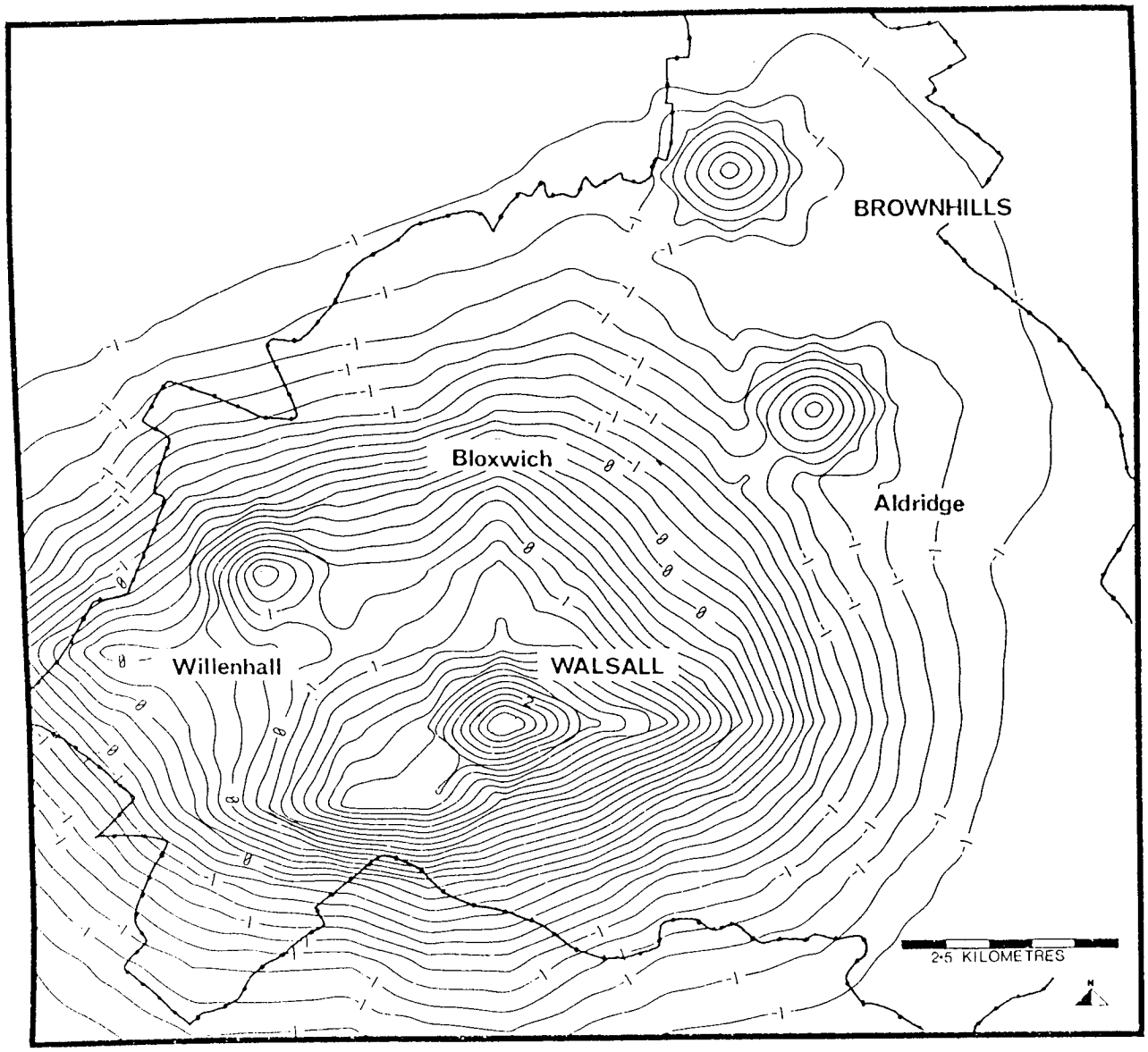


FIGURE 7.9 CONTOUR MAP OF PREDICTED IRONFOUNDRY FACTOR DEPOSITION IN THE WALSALL STUDY AREA.

FIGURE 7.10 ISOMETRIC PROJECTION OF PREDICTED IRONFOUNDRY DEPOSITION IN THE WALSALL AREA.

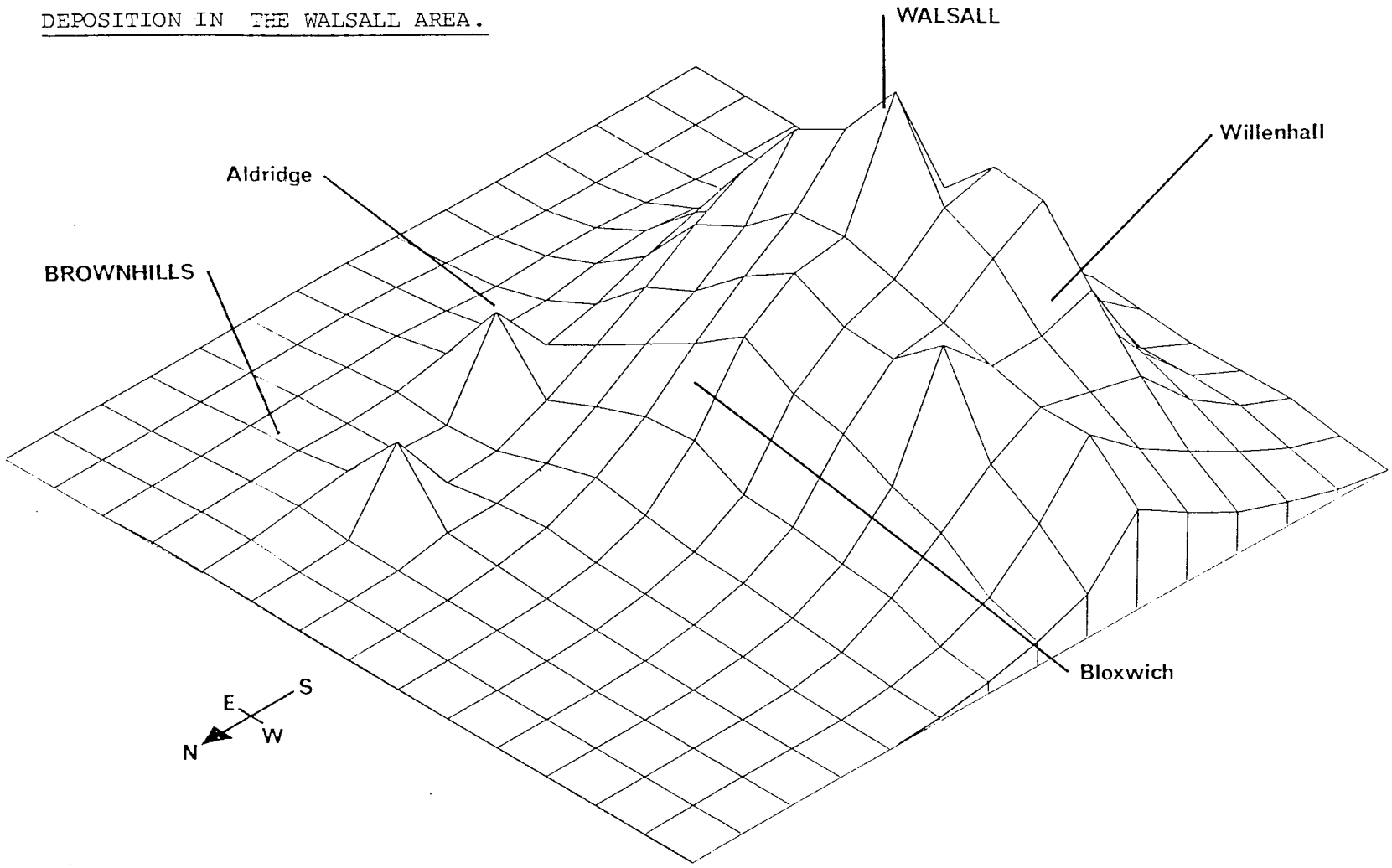
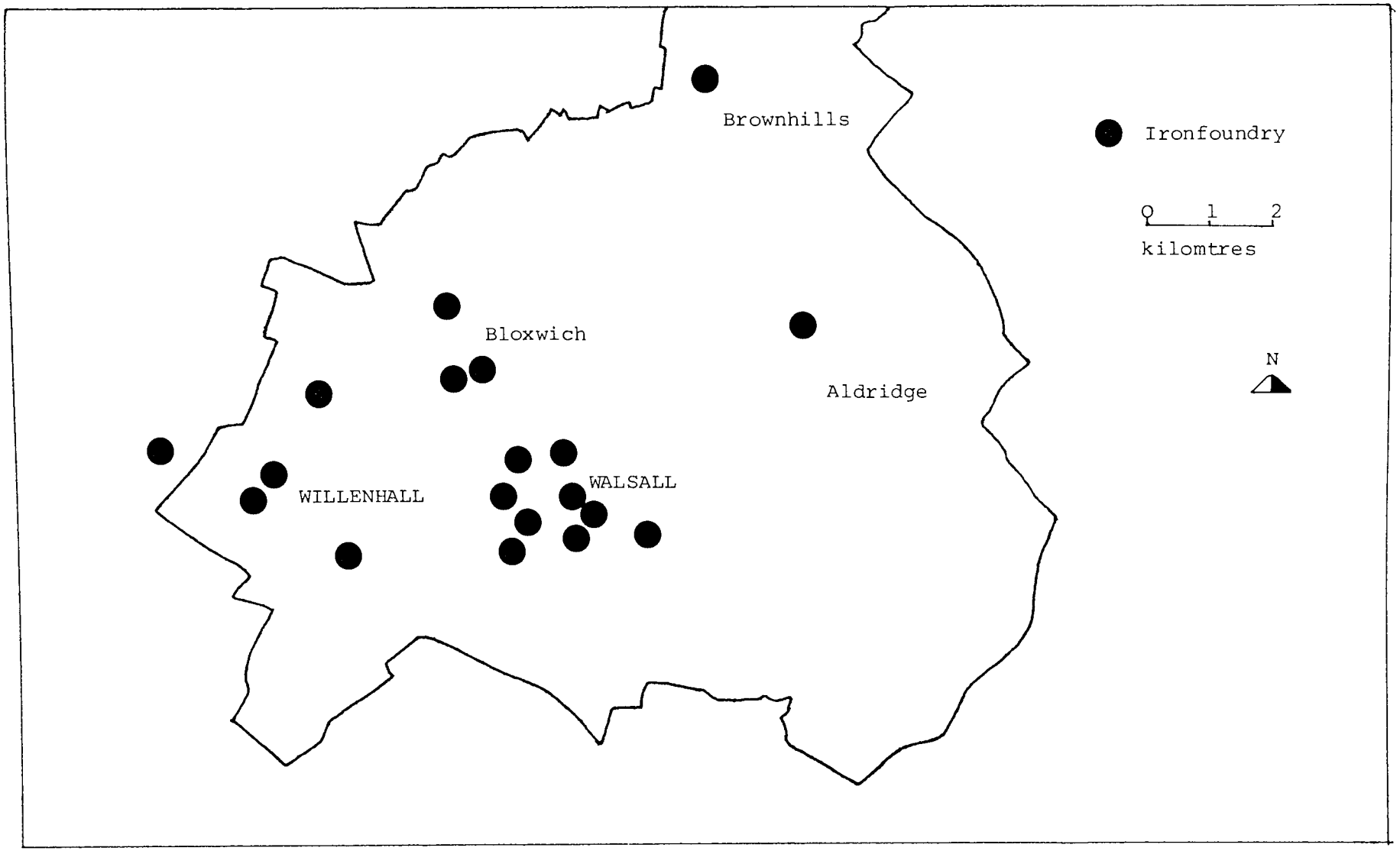


FIGURE 7.11 Location of Ironfoundries in Walsall during the survey period.



The presentation of the results of the model predictions in this graphic form allows the methodology to be used in an urban policy context, particularly pollution planning. The model is based on simple parameters relating to industrial activity and meteorological conditions and as such the effect of changes in these parameters can easily be investigated. This is most relevant for evaluating possible strategic alternatives for long-term reduction of pollution at source.

7.5 Conclusions

7.5.1 Source identification

Multivariate factor analysis has been shown to be a powerful technique for identifying sources of metals in deposition. Six factors have been identified which together account for 88.2% of the total variation in the deposition measurements. The six factors have been interpreted as representing coal combustion, vehicle/roadway sources, ironfounding, copper refining, metallurgical/general urban sources, and copper refining/ironfounding. Better separation could be achieved, particularly for the last two source types, if a greater number of elements were included in the analysis. These six source types are identified on the basis of common variance in the data set. Sources that are associated with spatially constant deposition levels are not identified by this technique.

Cluster anlaysis has been used to examine the spatial associations between deposition of certain elements and their possible sources. At a general level the cluster analysis technique can be used to separate areas into broad classes of deposition, such as those characteristic of rural or urban areas. Cluster analysis based on site deposition levels illustrates how deposition is spatially distributed in Walsall. For example, the central areas of Walsall/Pleck are observed to have elevated deposition levels of lead and cadmium while the rural/residential areas of the Borough have low lead and cadmium deposition rates. A further extension of the cluster analysis technique has been to use factorscores. This enables the provisional interpretation of factors to be checked

against the spatial distribution of a factor and its hypothesised source. Using this joint application of the Cluster and Factor models, the elevated deposition of both lead and cadmium noted in the central Walsall area (illustrated in figures 6.5 and 6.6) has been explained in terms of a combination of deposition arising from road/vehicles, copper refining, ironfounding and coal combustion.

Receptor models are limited by their mode of operation (i.e. they are explanatory). This chapter has demonstrated one way that the power of a receptor model can be extended by incorporating the factors in a predictive source model. In this way the nature of the deposition process can be examined in circumstances that are currently beyond the scope of the 'classic' source-based dispersion model. The ironfounding industry has been taken as the basis of this development application. However, the general factor modelling approach could be extended to other sources and even to other types of environmental media (e.g. air pollution, water pollution or even soil pollution). Using factors instead of variables means that the model predicts relative impact of sources rather than absolute impact. This is because factor analysis is concerned only with the variance of metal deposition rates, not with the absolute deposition of a specific metal. 'Q-type' factor analysis could be developed to provide quantitative estimates if total mass deposition rates were available and determination of bulk matrix components was introduced into the analysis. However, despite this limitation on using factors as the basis of a model, the technique represents a powerful tool that can potentially be used to study the problem of heavy metal pollution is a wide variety of situations.

CHAPTER 8

RESEARCH SUMMARY, CONCLUSION AND RECOMMENDATIONS

8.1 Summary and Conclusions

8.1.1 Summary of the research context and structure

This thesis has described the background to the scientific debate over the potential health effects of long-term population exposure to heavy metals, particularly to lead and cadmium. This debate has highlighted the important pathways through which metals released by anthropogenic activity may eventually reach man. It has been demonstrated in the thesis that the deposition of heavy metals in airborne particulate matter has recently been identified as one of these potentially important pathways, and one about which comparatively little is known (Royal Commission on Environmental Pollution, 1983, reporting on human exposure to lead, and the Commission of the European Communities, 1981, reporting on cadmium).

This research has focussed on the problem of deposition of heavy metals and this thesis has reported on the progress and achievements that have been made in pursuance of the specific research aims that were set out at the start of the research project. To recapitulate, these were:

- to explore the deposition measurement process and to develop and evaluate a deposition measurement method that is suitable for large scale surveys in urban areas.

- to explore the levels and spatial variability of heavy metals in deposition in urban areas.

- to investigate the relative significance of different sources of heavy metals, in deposited particulate matter.

The remainder of this chapter comprises of a summary and conclusion of the research in relation to these aims, followed by recommendations for further research.

8.1.2 Measuring heavy metal deposition in urban areas

There are two standard deposition measurement instruments currently employed in deposition monitoring surveys in the U.K. These are the Standard British Deposit Gauge (B.S.1747: Part 1) and the International Standards Organisation gauge (I.S.O Draft Standard ISO DIS 22/82). Both standards necessitate the use of sampling instruments which are bulky, require elaborate support frames, have special siting requirements and are expensive to purchase and maintain. These practical and technical difficulties have severely limited the number of sites that can be included in surveys of deposition in urban areas. In some cases there has been a move towards simple alternative methods. But these tend to be either qualitative (eg moss bags) or there are questions regarding the technical validity of the siting strategy adopted for surveys in urban areas eg 'jam - jars' on window ledges. Where the more rigorous standardised methods are used in surveys the practical and technical difficulties restrict the number of sites that can be included and as a consequence the scientific investigation of urban deposition has tended to focus on specific problems, such as

deposition around large identifiable sources. Very little information is therefore available on the typical ambient deposition levels or on the spatial variability of deposition across urban areas.

This research has identified the short fall in the measurement of deposition and has responded by developing a sampling instrument that is ideally suited for use in large scale surveys of urban areas. The main conclusions relating to the deposition measurement process are:

(a) The deposit cannister sampling technique avoids many of the traditional difficulties associated with monitoring of deposition in urban areas. The sampling instrument is cheap, light and easily constructed and can be sited without the normal restrictions associated with current techniques. The siting height (typically 6 metres as opposed to 1-2 metres for the standard techniques) minimises the problems of security and vandalism and reduces the possibility of contamination by locally resuspended dust.

(b) The reproducibility of deposit cannister measurements has been investigated using the technique of replication. The results of this investigation show that the reproducibility of the deposition measurements is not affected by the type of ambient environment the cannister is situated in. For lead, deposition rates can be measured to a precision of $\pm$ 0.123 mg/m^2/30 days($p = 0.68$) and for cadmium deposition can be measured to a precison of $\pm$ 0.015 mg/m^2/30 days ($p = 0.68$)

(c) The reproducibility of deposition measurements obtained using the deposit cannister has not been rigorously tested against that of the standard ISO gauge. However on the basis of an initial appraisal the reproducibility of deposit cannister appears to be at least as good as the ISO gauge. The relative accuracy of the two techniques has not been investigated.

(d) The reproducibility of the deposition measurements is limited by measurement error. This is composed of two separate component errors: the first relates to the physical efficiency of the process of collecting falling particles (instrument error) and the second derives from the analysis of metal levels contained in deposition samples (laboratory and analytical error). In this research atomic absorption spectrophotometry has been used as the main analytical tool. The precision of this method has been shown to be independant of the concentration of metals in deposition samples. For lead, analytical error explains 26% of the variance associated with deposition measurement. For cadmium however, analytical error accounts for 64% of the observed variance associated with deposition measurement using the deposit cannister.

The accuracy of the analytical procedure has been shown to be dependant on the concentration of metals. For lead 62% of the total quantity of metal present in a deposition sample is recovered during analysis, for cadmium however, 73% of the total metal present can be recovered.

(e) The deposit cannister technique is valuable for intensive surveys of urban areas; however in certain cases very high sample densities

may be required. This research has used a novel technique for achieving high sample densities bases on sampling a fresh snow surface, although this technique has obvious limitations in temperate latitudes.

8.1.3 Spatial distribution of heavy metals in deposition in urban areas

There is a large body of data on worldwide deposition, obtained from measurements made at single sites in various types of environment. From these data it is possible to identify broad ranges in deposition rates, varying from hotspot areas around major sources to the natural background levels in the polar regions. However very little research effort has been directed towards characterising the nature of ambient spatial distribution of deposition in urban areas. Arguably these areas are where the problem of human exposure to heavy metals is most acute. The development of the deposit cannister means that the nature of ambient urban deposition can now be investigated. This research has used this measurement technique to characterise deposition of lead and cadmium through a case study investigation of Walsall comprising 250 individual observations. The conclusions of this investigation are:-

a) The statistical distribution of the data set on deposition rates within Walsall is best described by the lognormal distribution. Therefore, statistics based on the sample of 250 deposition observations should be derived from logtransformed data. Thus, the average deposition of lead in the Walsall area over the six-week survey period is best described by the geometric mean of 1.38

$mg/m^2/30$ days with a 95% probability range of 0.23 - 8.11 $mg/m^2/30d$. The average cadmium deposition rate has a geometric mean of 0.05 $mg/m^2/30$ days with a 95% probability range of 0.01-0.21 mg/m^2 30d. The range in the deposition rate for lead covers 4 orders of magnitude, from 0.03-51 $mg/m^2/30$days. Cadmium deposition rates cover 2 orders of magnitude from 0.01-0.64 $mg/m^2/30$ days.

b) The sample of 250 individual measurement sites were located within twenty-seven $1Km^2$ grid squares (average 9 sites 1sq. Km.) The measurements within these $1Km^2$ areas are also lognormally distributed. The lowest $1Km^2$ area averages (geometric means) of 0.6 $mg/m^2/30$days for lead and 0.02 $mg/m^2/30$ days for cadmium were observed in areas of rural land-use. The highest $1Km^2$ average of 4.6 $mg/m^2/30d$ for lead and 0.11 $mg/m^2/30$ days for cadmium were located in the central urban area of the Borough near to industrial sources. There is a general association between the type of land-use and the levels of lead and cadmium deposition.

c) The average levels of lead and cadmium deposition observed in this survey are within the range reported in previous surveys of urban areas. When compared against the deposition standards used in West Germany, 0.3% of the borough exceeds the maximum standard for lead and 4.0% exceeds the maximum standard for cadmium deposition. When compared to the guidelines for food cultivation 1.8% of the borough exceeds the guideline level for lead deposition and 32.0% the guideline for cadmium. Evidently cadmium deposition is potentially a greater problem in Walsall than lead deposit ion.

e) The variability in the set of data on deposition rates in

survey arises as a result of two origins of variance; spatial variations occurring between measurement sites, and the variation introduced as a result of measurement errors. In the Walsall survey broad differences in deposition across the Borough area account for only a third of the total spatial variation in deposition rates. Variations within areas of about one square kilometre are a more important source of variance. Even within areas as small as $100m^2$ there are significant variations in deposition. For cadmium, the greater part of this variance is due to measurement error in contrast to lead for which measurement error is not significant.

The observed spatial variation in deposition over comparatively small areas ($>1Km^2$) are assumed to reflect the heterogenous nature of the urban environment and the localised effects of many small sources.

This raises questions over the spatial representativeness of the single deposition measurements typically used in previous surveys of urban areas. The deposit cannister provides a practical solution to this problem as it enables comparatively large sample densities to be achieved at low cost.

f) The investigation of the distribution of fallout originating from an industrial source of heavy metals (a large secondary copper refinery) has confirmed that deposition follows an exponential decay with distance downwind and approaches background within a distance of 1Km. The results of a deposition modelling exercise for ironfoundry emissions have also confirmed this rapid decay with distance.

8.1.4 Identifying sources of heavy metals in deposition

Walsall, like many urban areas in the United Kingdom, is a complex mixture of land-uses, many of which are associated with heavy metal emissions. Walsall has been shown by previous research to be an area which is generally contaminated by heavy metals; cadmium in particular. The metal industries have frequently been implicated as a major contributor to this contamination but up until now no direct evidence has been available to substantiate his hypothesis. From the viewpoint of local pollution control policy this represents a considerable weakness in the scientific response to the problem that exists in the Borough. This research has explored various ways by which this source identification can be achieved in the case of heavy metal deposition. The main conclusions relating to the source identification procedure are:

a) Receptor based modelling techniques represent a viable alternative to the more traditional source-based models. However in contemporary scientific research their development and widespread application has been largely restricted to the field of air pollution. This research has successfully developed two multivariate receptor models for use in identifying sources of heavy metals in deposition.

b) The first multivariate receptor model was based on the statistical technique of Factor Analysis. The factor model indicated that six factors or source influences accounted for 88% of the variance in deposition levels in Walsall. These factors have been interpreted as follows:

Crustal emissions (mainly coal and coke combustion),

road/vehicle sources, ironfoundry emissions, seconday copper refining a general metallurgical/urban source and a copper refining/ironfoundry source.

c) A second multivariate receptor model based on Cluster Analysis has been developed and used for two purposes; firstly to examine the geographic associations between deposition and known sources; and secondly as an aid to interpreting the factors. These cluster models have substantiated the provisional interpretations of factors and also demonstrated that the elevation in levels of lead and cadmium deposition in the central Walsall area can be explained by emissions from Copper Refining, Ironfoundry, Road/Vehicle emissions and coal conbustion sources. However, a major weakness of the factor analysis model is that it explains variance rather than absolute deposition levels. As such it is not possible to quantitify how much of particular deposition level is explained by any specific point source.

d) A further extension ot receptor modelling has been to incorporate factorscores (a relative measure of the importance of each factor at each measurement site) into the traditional technique of dispersion/deposition modelling. By calibrating a source-based prediction model against the factor hypothesised to relate to the ironfoundry industry (in other words, using factorscores as the dependent variable) it was possible to examine the dispersion/ deposition process in a complex environ ment (multisource urban area). This model was expressed in the form of a distance-decline function which was linked to a simple emission inventory for ironfoundry mass emissions. The influence of windspeed and

directional frequency were taken into account. In a calibration exercise 71% of the observed variance in the ironfoundry deposition factor was reproduced by the simple prediction model. This evidence supports the hypothesised interpretation of this factor.

e) The emission inventory for ironfoundry emissions in the entire West Midlands area has shown that these may represent an important source of lead emissions to the atmosphere. Based on data gathered in 1982, over 70 tonnes of lead are estimated to have been discharged from the ironfoundry cupola furnaces (reported in Appendix A).

g) While this thesis has concentrated on the specific problem of source identification for metals in deposition, many of the technical matters and source tracing techniques are readily applicable to other environmental media (eg urban dusts, air pollution, soils, urban runoff etc). The growing public and scientific concern over the question of widespread contamination by toxic metals creates the demand for source tracing methods, for while much research has concentrated on measuring the levels of metals in the environment only in a few cases have the sources of elevated levels been positively identified.

8.2 Recommendations for further research

8.2.1 Summary of recommendations

Several areas of further interest have arisen from this research and represent areas of potential future research. These are outlined below.

a) There is a need for further detailed evaluation of the performance of the deposit cannister, including:

- comparision with ISO gauge
- effect of siting height and the problem of resuspended dust contamination
- effects of varying gauge aperture and exposure periods

b) This research has relied on only ten variables as the basis of the factor analysis. The source-resolving power of the technique would be strengthened by using a larger number of variables. Additional elements should be selected on the basis of their association with specific sources (eg calcium-cement, sodium - sea salt, vanadium - oil combustion, selenium - coal combustion, bromine - petrol combustion etc).

c) Factor analysis can be used on data collected from a single site but with observations that vary over time. Therefore it would be possible to use this technique to identify source influences at individual sites currently used for continuous monitoring (for example A.E.R.E Harwell maintain a 'background' monitoring site at Wraymires, Cumbria). Future environmental surveys should be designed with source identification in mind (ie multi elemental determinations).

d) The factor and Cluster Analysis techniques are both readily applicable to other environmental media, eg airborne particulate matter, urban dusts, soils, urban runoff, sediments etc.

e) The source-based deposition model used in this research is relatively simple. Reliability and range of applications may be increased by the use of more complex models involving more meteorological parameters and which take into account such aspects as discharge height and even fugitive emissions. Long-range transport and deposition may even be considered.

f) This research has concentrated on metal levels in deposition and transfer pathways from sources. However an important aspect of the human exposure problem is the subsquent addition of metals to soil and dusts. The impact of deposition on levels in these media is obviously an important dimension of the human metal exposure problem and should be considered as a priority area for further research. For example in the vicinity of the secondary copper refinery studied in this research deposition appears to be at a sufficient level to cause long-term accumulation in soils in the area.

j) When the role of deposition as a source of metals in soils and dust and subsequently in food is better understood it should be possible to identify what levels of metal input to thse media are acceptable for the long-term protection of human, plant and animal life in much the same say that is currently done for metal input to soil in sewage sludge, and for deposition in the F.D.R.

k) The compilation of an emission inventory for ironfoundries for the West Midlands has identified a potentially important source of lead to the environment. In the U.K, metal emission inventories are not widely used for local and national policy purposes, however the ironfoundry inventory clearly demonstrates the important role that these could fulfil. There use in other situations should be considered as a tool in identifying possible sources of localized problems.

APPENDIX A

'ESTIMATING HEAVY METAL EMISSIONS FROM IRONFOUNDRY CUPOLA FURNACES'.

Reproduced from 'Clean Air' vol.12(4) pp 127-137. Paper summarises the emission inventory method which was used to compile the Walsall foundry inventory.

Table A1 contains an update on the number of Cupola furnaces in the West Midlands Region for 1984.

ESTIMATING HEAVY METAL EMISSIONS FROM IRON FOUNDRY CUPOLA FURNACES

by
S.A. Simmons

The ironfounding industry of the West Midlands has long been linked with air pollution problems. The confinement of a large number of cupola furnaces within a small geographical area known as the 'Black Country' (Figure 1) acts to multiply the effects that their emissions have on air quality. This paper examines one aspect of the air pollution problems associated with cupolas, namely the heavy metals present in grit, dust and fume emissions. A simple heavy metal emission inventory has been compiled for the West

ativeness of a reading taken only during the middle period of a melt cycle, i.e. after start-up and before blow-down [3].

ii) *Representativeness between types:* the cupolas in the West Midlands vary widely in size, operation, charge make-up and pollution abatement facilities. Obtaining samples from some of the small but common cupola types would be difficult.

Because of these difficulties a different method of determining the quality and quantity of cupola emissions has been devised.

Table A 1

UPDATE Position for 1984

This table provides an upto date summary of the number of cupola furnaces in the West Midlands area and also extends the inventory to include foundries from the West Midlands Region.

Area	Number of Cupola Furnaces in Area			
	Total	below 3 tonnes	3-10 tonnes	>10 tonnes
Dudley	42	24	15	3
Sandwell	48	11	28	9
Walsall	26	2	24	-
Wolverhampton	12	4	6	2
Birmingham	2	-	-	2
	(130)	(41)	(73)	(16)
Cannock	2	2	-	-
Coventry	6	-	6	-
Lichfield	2	-	-	2
Nuneaton & Bed.	2	-	-	2
Rugby	2	-	-	2
Stratford	2	-	2	-
Warwick	2	-	2	-
Worcester	1	1	-	-
Wrekin	20	3	17	-
	(41)	(6)	(29)	(4)
TOTAL	169	47	102	20

Data obtained from The National Society for Clean Air Working Party on Emission of Lead from Ironfoundries.

APPENDIX B

'Technical issues relating to the laboratory procedure for analysing heavy metals in deposit cannister samples'.

Technical issues relating to the laboratory procedure for analysing heavy metals in deposit cannister samples

B.1 Summary of the analytical method

B.1.1 Outline

This appendix gives detailed technical and procedural information relating to the analysis of heavy metals in deposit cannister contents following exposure for approximately 30 days. This first section, B1, gives a technical description of the analytical techniques, instrument settings etc. The second section, B2, discusses the experimental procedures that have been used to investigate experimental analytical errors. The last section, B3 examines in detail the types of error that may occur with the method of Atomic Absorption Spectrophotometry.

B.1.2 Technical description of the analytical method

The investigation of trace heavy metals in a given medium requires sensitive and precise techniques. The classical methods alone do not usually provide a solution to determination of concentrations of metal species to the parts per million (p.p.m) levels. Therefore, more sensitive instrumental methods are now widely used. These highly sensitive techniques normally require samples to be pretreated, usually to eliminate interfering substances and also to bring the elements being studied into the concentration range and chemical state required for the analytical detection system.

In this research determination of low levels of heavy metals in deposition samples was achieved using the popular and the highly sensitive technique of atomic absorption spectrophotometry. This instrumental detection method was chosen on the grounds of practicability, ie mainly that it was readily available within the University of Aston.

There are two basic stages to the atomic absorption spectrophotometric method: firstly, pretreatment by Mineralisation and solubilisation of metals present in samples containing organic fractions was achieved using nitric acid digestion; secondly, determination was then conducted by the application of atomic absorption spectrophotometric analysis. The analytical process was conducted in five stages. These were:

1) Samples collected in the field were returned to the laboratory in sealed deposit cannisters. These were opened, acidified with approximately 1ml of 'Aristar' grade nitric acid (HNO_3) and then re-sealed and stored in a cool place.

2) The cannisters were re-opened and the volume of water within the cannister was measured using a measuring cylinder. The remaining insoluble fraction was washed and wiped using a cellulose ashless filter paper into a 50ml Kjeldahl flask. The rainwater fraction was also added to the flask in aliquots of 20ml which were successively evaporated in a heating rack. The final aliquot was evaporated to dryness and allowed to cool.

3) The flasks were then transfered to a fume cupboard where 5ml of 'Aristar' grade HNO_3 was added. They were then slowly heated until red/brown nitrogen dioxide fumes were evolved. The temperature was

slowly increased to evaporate off successive additions of HNO_3. When all organic material was digested the samples were slowly boiled to dryness, when cool 2ml of HNO_3 was added to solubilise the mineralised metals.

4) The flask contents were washed and filtered into a 10ml grade 'A' volumetric and made to volume with distilled water. The digested samples, now in 20% HNO_3, were then transfered to glass sample tubes and stored in a cool dark place awaiting determination.

5) When all samples had been digested the metal concentration in each sample was measured using an atomic absorption spectrophotometer calibrated against appropriate standard solutions.
All samples were analysed together to minimise problems of intercomparability. All metals were determined using flame absorption spectrophtometry, except for arsenic which was determined using hydride generation. The following analytical standards (ug/ml concentration) were prepared in 20% HNO_3 (matrix matched) from stock solutions of 1000 ug/ml:-

Standard	Al, Cu, Fe, & Pb	Cr	Cd, Mg, Mn, & Zn
Top	20	10	2
Middle	10	5	1
Bottom	5	2	0.5
Blank	0	0	0

Standards for hydride generation of arsenic were prepared to 1.0 ug/ml in 10% v/v HCl.

The atomic absorption spectrophotometer was a Perkin-Elmer 560 research grade instrument with deuterium arc background correction. Hollow cathode lamps were used for all metals set to the following conditions:-

Element	Slit	Wavelength (nm)	Flame
Al	0.7	309.3	N_2O/C_2H_2
As	0.7	193.7	Air/C_2H_2
Cd	0.7	228.8	Air/C_2H_2
Cr	0.7	257.9	N_2O/C_2H_2
Cu	0.7	324.8	Air/C_2H_2
Fe	0.2	248.3	N_2O/C_2H_2
Pb	0.7	217.0	Air/C_2H_2
Mg	0.7	285.2	Air/C_2H_2
Mn	0.2	279.5	Air/C_2H_2
Zn	0.7	213.9	Air/C_2H_2

Where necessary samples were diluted with 20% HNO_3 using an automatic diluter. Results were obtained as a concentration per volume of sample and these were then expressed as a deposition rate per unit area normalised to 30 days.

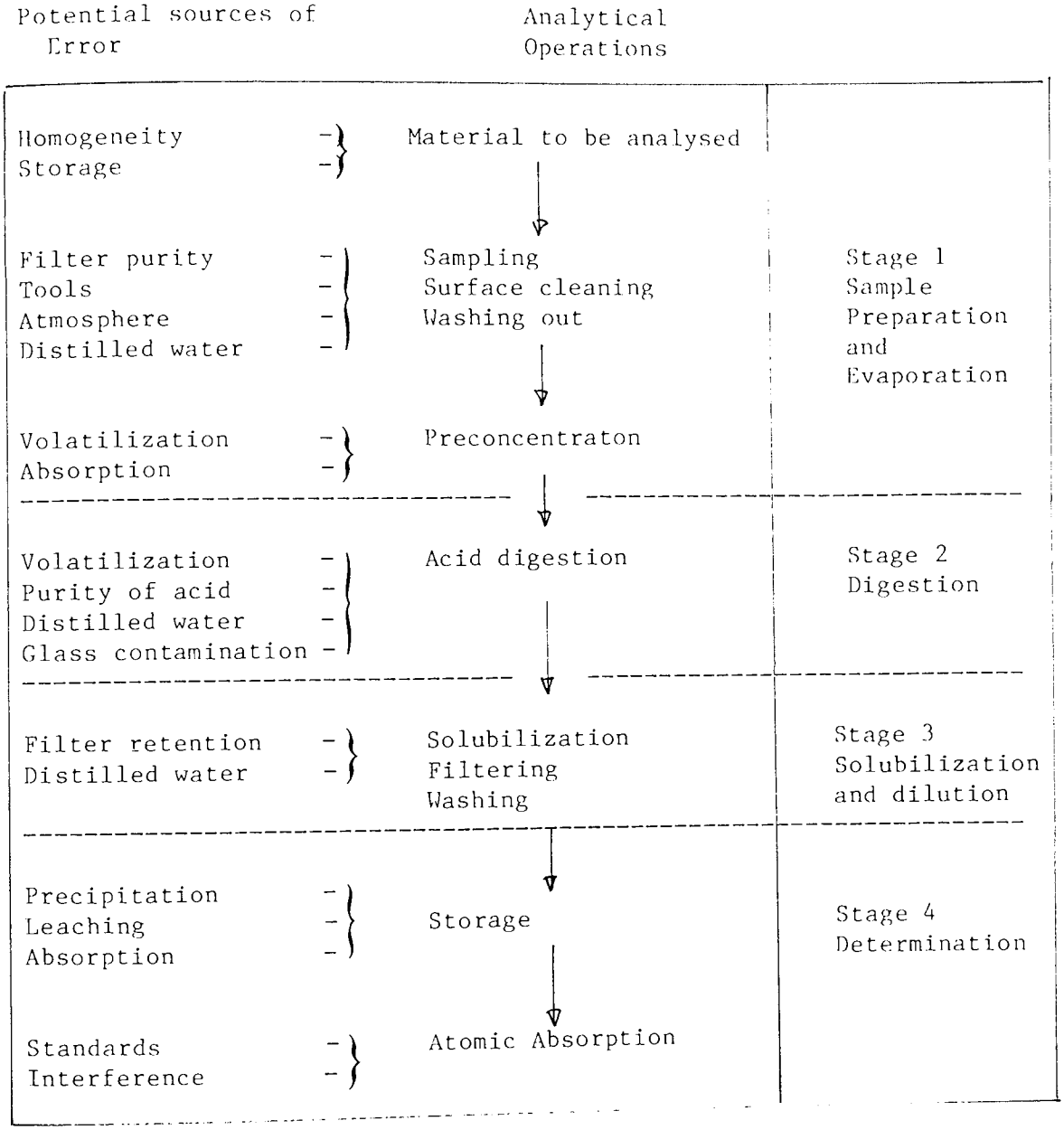
B.2 Experimental procedure for estimating analytical accuracy and precision

B.2.1 Experimental design

This section gives supporting information for chapter 5 of the main text regarding the experimental investigation of analytcal error. This investigation was conducted by analysing samples whose concentrations of component metals were either zero or some known positive concentration. By analysing a number of replicated samples a sample mean, $\overline{C}$ and standard deviation σ_c could be calculated. Two basic experiments were used; the first consisted of analysing samples of a positive concentration to enable the error involved in analysing deposition samples to be estimated. The second involved introducing blank analytical control samples into various stages of the experimental procedure to evaluate the significance of each stage a source of both random error and bias (contamination)

In the first experiment two sets of samples were analysed separately. The first set of samples consisted of six sub-samples of a 1.0 ug/ml concentration of each metal added to empty deposit cannisters. These were treated as deposit samples and analysed in the normal fashion. The second series of samples consisted of a set of four batches of six replicate samples. These consisted of four concentrations of lead, magnesium and copper; 0.5, 1.0. 2.0 and 4.0 ug/ml, giving a total of 36 samples. These were designed to investigate how analytical error changes with changes in concentration.

Figure B1 General outline of the stages in the analytical process and the errors that may affect each stage



The microanalytical process is a complex series of dicrete analytical operations, pipetting, digesting etc. To understand how each of these stages affects the error of final determination a second experiment was conducted where a series of blank samples were introduced at key steps in the analytical process. This is represented in Figure B1 where the analytical procedure is represented as a series of stages. Six blank samples were introduced at each stage. The analysis of the results of these two series of control experiments are discussed in chapter 5 of the main text.

B.3 Error associated with atomic absorption spectrophotometry

B.3.1 Introduction

The method of atomic absorption spectrophotometry is based around the detection instrument, i.e atomic absorption spectrophotometer (A.A.S). The performance of this instrument will dictate how the method as a whole functions as an analytical technique. This section examines the detailed experimental investigation into the performance the A.A.S.

B.3.2 Sensitivity, Noise and detection limit

The A.A.S is characterised by a particularly complex functional structure which includes chemical, electrical, mechanical and optical elements. All of which may vary randomly and systematically with time. Random variations cause instrument noise which affects the sensitivity and detection limit. Systematic changes lead to changes in response or increases in bias over time.

Instrumental detection limit is governed by the sensitivity and the signal/noise ratio for an element. Elements having low background noise levels such as copper can be determined relatively precisely compared to elements having greater sensitivities but higher noise levels such as cadmium. This relationship between instrument noise, signal and detection limit is illustrated in Figure B2 in which a) has a lower detection limit than b).

Sensitivity is expressed in the response function $y = f(c)$ which has been found to be constant only over a limited range of

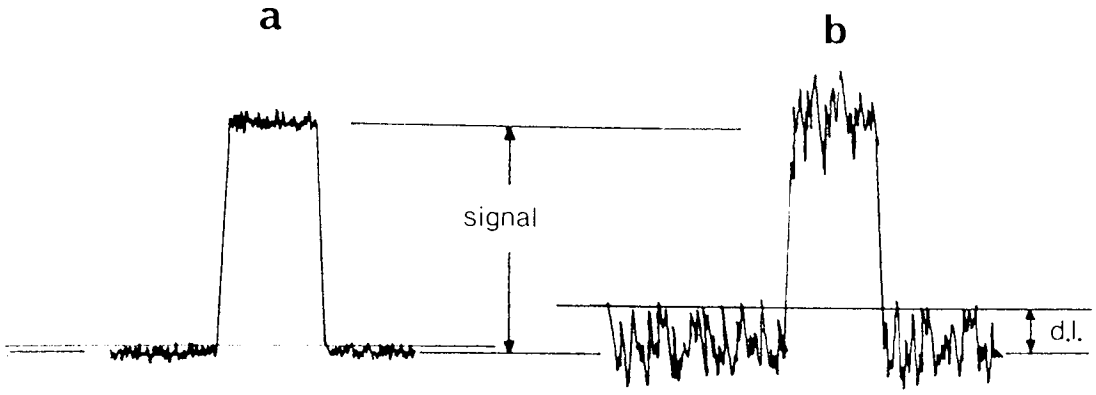


FIGURE B2 Instrument signal/noise ratio and sensitivity. (both metals have the same sensitivity but (a) has a greater signal/noise ratio than (b).

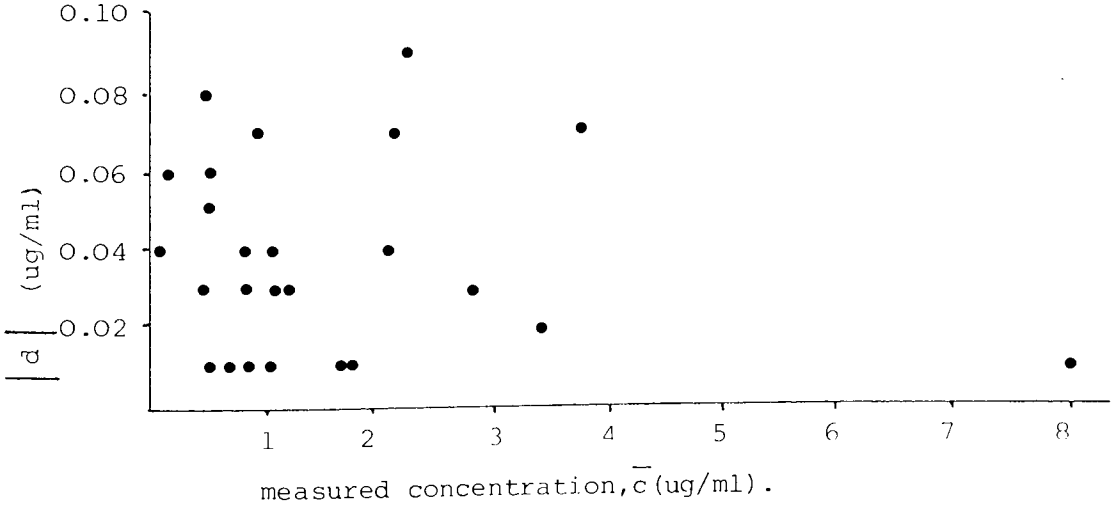


FIGURE B3 Graph illustratingthat absolute difference |d| between repeat measurements of a sample are independant of concentration.

concentrations which are termed the Linear range. Above this range sensitivity decreases with increasing concentration. All determinations are more precise when conducted within the linear range of the response function.

The detection limit (d) of a particular element is defined on the basis of statistical criteria. Instrument noise has been found to be normally distributed (eg Liteanu and Rica, 1980), therefore repeated readings at machine zero provide estimates of instrument noise expressed as a standard deviation σ_4 (Younden, 1952). This can be used to define d.l using the relation

$$d.l = K\sigma_4$$

In this research K has been taken as 2 which gives a 5% probability of a zero reading being interpreted as a positive sample reading. This d.l does not correspond to the mimimum concentration detectable with certainty (K = 6) and in this sense d.l is not a measure of the detection capacity. Estimates of instrument noise, σ_4 and d.l derived from repeated zero readings are given in Table B.2. These estimates of instrument noise are used as the basis for the investigation of analytical error in the main text in section 5.3

Table B.2 Background noise, σ_4 and detection limit, d.l for the study metals determined by flame aspiration, n = 10

Element	σ^4 (Ug/ml)	d.l (ug/ml)
Pb	0.02	0.04
Cd	0.003	0.006
Al	0.4	0.28
As	-	-
Cr	0.02	0.04
Cu	0.006	0.012
Fe	0.258	0.516
Mg	0.02	0.04
Mn	0.025	0.05
Zn	0.014	0.028

These d.l's were used as the criteria for assessing whether levels were detectable during the main analysis programme for deposit cannister samples.

The estimates of σ_4 were made at machine zero, i.e ideal conditions which represent the background instrument noise. In practice noise may increase or decrease with increasing concentration. This was investigated by making repeat measurements of samples selected at random during the analysis of deposition samples. The differences in concentration between two independent measurements are a measure of the noise at a positive concentration. This noise can be expressd as a standard deviation σ_s[1]. The mean difference $\bar{d}$ between two readings in K samples gives a measure of instrument drift. In the absence of drift $\bar{d}$ should be equal to zero. The results of a series of repeat measurements are summarised in Table B3. The t-test shows whether the observed difference $\bar{d}$ is statistically different from zero. The F-test indicates whether the variations at a positive concentration, σ_s, are statistically greater than those observed at machine zero, σ_4. These results show that for lead and cadmium there are significant increases in noise and significant bias. For both metals the bias is positive indicating an overall decrease in sensitivity during the analytical run. However, this decrease is of only minor significance (indicated by relatively small value of $\bar{d}$) and can be disregarded as a general source of error to the final results.

---

1. Noise, σ_s is calculated as the standard deviation of the difference, di, between repeat readings of a series of K randomly selected samples

$$\sigma_s = \left(\sqrt{\sum_{i=1}^{K} \frac{(d_i - \bar{d})}{K - 1}^2} \right) \Big/ \sqrt{2}$$

Table B3 Results of repeated measurements of randomly selected samples

	K	$\bar{d}$	σ	t	F
Pb	25	0.03	0.038	**	*
Cd	18	0.008	0.015	*	**
Al	18	-0.2	0.527		**
Cr	19	0.128	0.065	**	**
Cu	27	0.025	0.021	**	**
Fe	19	0.305	0.559	*	*
Mg	20	0.017	0.146		**
Mn	18	0.056	0.063	**	**
Zn	19	-0.28	0.614		**

* p 0.05 ** p 0.01

These repeat readings can also be used to investigate the distribution of noise at a range of concentrations. This is achieved by plotting the absolute difference between the repeat readings against the concentration in the sample. For both lead and cadmium the random variation d were found to be independant of concentration as shown by the example in Figure B3. This suggests that the increase in detection noise over that of the background white noise, σ_4 is caused by some characteristic of deposition samples which is not dependent on the concentration of metal, ie interference by other chemical components of samples not present in the controls. In general chemical interference can be minimised by matrix matching samples and standards. However, the variability of the composition of samples is such that matrix matching cannot be exact, particularly with respect to levels of alkaline and alkali earth metals such as sodium or calcium.

APPENDIX C

'Measurement of heavy metal fallout using a flat snow surface in the vicinity of a secondary copper refinery'.

Reproduced from 'Environmental Health' Jan 1983 pp20-23
Paper summarises the study of localised deposition in the vicinity of a prominent industrial source.The results of the survey are also considered in section 6. of the main text.

Measurement of Heavy Metal Deposition using a flat snow surface in the vicinity of a secondary copper refinery.

S. A. Simmons.

University of Aston in Birmingham.

1. Summary

This paper reports the results of an investigation into the dry deposition of airborne matter containing heavy metals in the vicinity of a secondary copper refinery in the West Midlands. An original feature of the study is the use of a snow surface as a short-term collector of dry deposition. This made possible a rapid collection of a large number of samples in locations where the use of deposit gauges would have been impracticable.

The results have shown the refinery to be a major source of heavy metals in the area. Over the sample period of 5 days, deposition in the vicinity of the refinery was up to 50 times higher than the general urban background. The deposition of lead was equal to or higher than that observed by the Warren Spring Laboratory in their recent study of various U.K. leadworks.

2. Introduction to the Study

The dry deposition of airborne particulate material containing heavy metals forms an important pathway through which industrial emissions of these potentially toxic substances can reach soil, crops, plants, and ultimately animals and man.

The measurement of dry deposition is however restricted by the difficulties experienced when using currently available techniques such as 'deposit gauges', where an assessment of short-term localised deposition around an important potential source is required, then considerable technical and practical difficulties need to be overcome to provide the necessary number of samples in the required locations.

As an alternative to current methods Forland and Gjessing (1975) made use of a fresh snow surface to collect deposition in rural and urban areas around Bergen in Norway. Dovland and Eliassen (1976) also used a flat snow surface to estimate the deposition velocities of sulphur and lead. In both of these studies considerable advantages were seen in using a snow surface as a 'fallout collector'.

In the climate experienced in the U.K. the ephemeral nature of snow-falls means that this technique has a more limited application than in Norway. In February 1981 however snow fell and remained largely unmelted for 5 days. This snowfall provided an unusual opportunity to carry out a detailed study of the dry deposition of airborne heavy metals orginating from a large secondary copper refinery in the West Midlands.

The refinery is located in an industrial urban area and had already been shown to be a major source of airborne metals, particularly copper, lead and zinc. Soil metal levels in the area are also higher than would be expetced when compared to similar soils some distance from the refinery. The Joint Unit for Research on the Urban Environment (JURUE) has conducted an extensive soil sampling and analysis programme which encompassed this area on behalf of the Local Authority Environmental Health Department (Pocock 1982) The refinery was clearly shown to be acting as a source of heavy metal soil contamination.

The study of snow contamination was conducted as part of the authors wider investigation into the sources of heavy metals in an industrial and urban area.

3. Methods

Samples of surface snow were collected after the snow had lain undisturbed for 5 days. The samples were taken on a north-south transect basis with transects being set at 0,250,750 and 1750 meters

westwards of the refinery. An identical set of samples on the up-wind side was planned but could not be taken due to an unexpectedly rapid overnight thaw.

Surface layers of snow were collected in $105cm^2$ samples and thawed to allow the levels of copper and zinc to be determined by atomic absorption spectrophotometry.

Meteorological data was obtained from the refinery where a continuous monitoring of wind speed and directions was made.

4. Results

The extent of contamination by dry deposition was clearly visible over the entire area to the west of the refinery. Surface dis-colouration ranging from light to dark grey extended through the top 0.5cm of the snow pack. The results of the analyses are shown in Table 1.

The levels of metals measured in the snow samples will consist of three identifiable components.

These are:
1. Rural or uncontaminated Background
2. Typical Urban Background
3. Copper refinery hotspot contamination

Samples taken directly downwind of the copper refinery will have a total heavy metal atmospheric fallout made up of the contributions of all three components. Sites out of the range of influence of the refinery fallout will have deposition characterised by the first two elements only.

In table 1 this is clearly shown; backgrounds from sources other than the refinery give approximate deposition levels of around

Table 1,a. Copper deposition at 44 sample sites downwind of a secondary copper refinery (mg m^{-2} 5 $days^{-1}$)

Station N to S	Transect Distance downwind from the refinery (metres) 1970	750	250	0
1	2.90	12.21	0.29	0.41
2	5.04	13.93	1.16	0.73
3	2.39	19.62	0.73	3.57
4	2.47	16.67	83.23	1.51
5	4.24	10.68	17.51	232.69
6	6.36	6.30	10.69	21.20
7	10.43	6.04	49.56	51.12
8	0.62	4.79	11.63	89.04
9	2.72	23.37	1.74	3.06
10	3.64	5.39		3.67
11	5.01	2.68	4.08	0.96

Table 1,b. Lead deposition at 44 sample sites downwind of a secondary copper refinery (mg m^{-2} 5 $days^{-1}$)

Station N to S	Transect Distance downwind from the refinery (metres) 1970	750	250	0
1	9.85	1.26	3.44	0.77
2	12.55	10.87	1.25	3.44
3	6.55	31.80	0.48	10.01
4	2.89	7.51	75.91	0.29
5	7.94	12.84	12.50	243.55
6	20.52	9.89	7.28	19.03
7	4.32	22.76	80.33	34.63
8	3.58	22.16	1.94	103.88
9	9.92	22.09	1.69	4.62
10	10.66	20.59	1.57	4.28
11	16.43	5.59		4.06

Table 1.c. Zinc deposition at 44 sample sites downwind of a secondary copper refinery (mg m^{-2} 5 $days^{-1}$)

	1970	750	250	0
1	38.53	10.99	3.88	13.13
2	21.47	41.21	4.39	2.32
3	15.85	129.91	1.52	27.81
4	1.90	33.51	266.20	4.56
5	11.75	32.03	128.69	1039.99
6	11.13	23.45	29.86	46.72
7	11.30	80.66	236.71	75.48
8	6.17	96.72	1.66	46.05
9	14.04	61.21	7.75	7.61
10	22.25	35.31	5.51	4.49
11	24.60	11.47	4.22	11.22

3mg m^{-2} 5 $days^{-1}$ for Copper, 5 mg m^{-2} 5 $days^{-1}$ for lead and 15 mg m^{-2} 5 $days^{-1}$ for zinc. Levels greatly in excess of these urban backgrounds can be assumed to be a result of deposition originating specifically from the refinery. At sites highly exposed to refinery fallout this may be as high 50 times greater than the urban background level.

5. Discussion: Significance of Results

Previous studies of heavy metal deposition have mainly concentrated on measuring monthly deposition rates by the standard method of the 'deposit gauge'. This means that direct comparison of the results of this 5-day study with the literature is difficult. In an effort to counter this the results of this study have in the particular case of lead, been converted to give a crude estimate of deposition over a month-long period at various distances from the refinery. To make this estimation an urban background deposition of lead of 5mgm^{-2} 5 $days^{-1}$ is assumed which corresponds to a monthly deposition rate of 30mgm^{-2} 30 day^{-1}.

Superimposed on this background are the effects directly attributable to the refinery, which we have analysed and expressed as

a classic 'power regression' model of the type $y = ax^b$ where y is the deposition rate in mgm^{-2} 30 $days^{-1}$ and x is the distance in metres from the refinery (a and b are constants). Calibrating this model on the data in Table 1b, we found that:

$$y = \frac{8500}{x} + 30$$

The predicted y values for deposition against distance from the refinery are plotted in Fig C1. along with data from the recent Warren Spring Laboratory Study of lead deposition around secondary lead works (Turner, Carroll and Barrett (1980)). There is substantial agreement between the two sets of data; deposition near to the refinery is at a level at least as high as the highest levels measured by Turner, Carroll and Barrett, and over short periods deposition appears to be even higher at points within the downwind fallout area.

In an earlier study of deposition around a similar secondary copper refinery also in Walsall (Cawse 1980), levels of fallout were also found to be of comparable magnitude to those found in this study, (see Table 2).

In his study, Cawse also estimated the potential addition of metals to the soil reserve in the area and compared them to Department of the Environment's guidelines (1977) for the maximum addition of metals to soil from sewage sludges. The results of this study are presented along with those from Cawse and the DoE Guidelines in Table 3, from which it can be seen that the area immediately next to refinery (50m) receives metals from fallout greatly in excess of the DoE recommendations.

TABLE 2. Deposition of Copper, Lead and Zinc compared to previous studies (mg m^{-2} 5 $days^{-1}$).

		Urban Sites*			Non Urban*	
	Range in Present Study	Walsall		Swansea Central	Wraymires Cumbria	Chilton Oxon
		Slaters Lane	Huckers Rd			
Copper	0.29-232.69	20.0	59.0	0.5	0.4	0.3
Lead	0.29-243.55	0.5	1.3	0.8	0.4	0.4
Zinc	1.52-1039.99	12.0	17.0	1.4	0.6	0.6

*From Cawse (1980). Converted directly from g/hectare/year to $mg/m^2/5$ days.

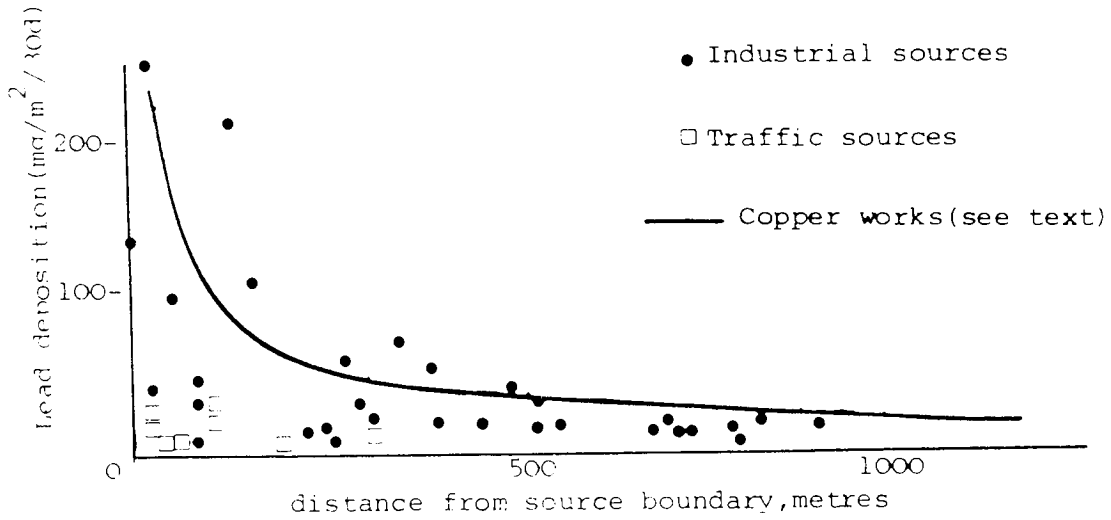


FIGURE C1 Lead deposition in the vicinity of lead and copper works.

TABLE 3. Estimated Accumulation of metals in soils over a 40 year period from deposition (kg hectare $^{-1}$)

Metal	DoE Guideline (Maximum)	Cawse 1980 Hucker Rd	Cawse 1980 Slater Lane	Present Study (distance) 50m	Present Study (distance) 1000m
Cu	280	1300	440	720	126
Pb	1000	28	11	720	126
Zn	560	380	270	2160	378

It is of further interest to find out what quantity of metal was deposited over the area of refinery fallout during the 5 day period. A crude approximation may be dreived by measuring the areas affected by refinery fallout, table 4.

The secondary copper refinery was only in productive operation for 36 hours during the 5 day period. So these quantities of metals were relased as fallout in only 36 hours. This is an approximate minimum hourly release of 2kg total metal (Copper, + Lead + Zinc).

TABLE 4. Total fallout of metals over the 5 day period

Metals	total deposition (kg)
Copper	11.2
Lead	9.0
Zinc	48.6

6. Discussion: Spatial Analysis of Results

From the results of this study it is clear that the refinery has a profound affect on the heavy metal deposition of the study area. The area of heavy fallout is limited to about 500m downwind of the refinery, but beyond this levels are still elevated above the urban background. A more detailed spatial analysis indicated that there are two separate plumes trending away from the refinery. One plume is of a limited lateral spread and could be the result of a bag filter fire, while the other broader plume is more likely to have resulted from general stack and fugitive emissions.

7. Discussion: Technical Issues

The snow surface technique used in this investigation is subject to certain limitations. The first is a function of the snow medium contamination by rainout and washout processes during the precipitation period. This inherent 'snow background' was determined for this study and found to be of negligible proportion compared to the levels measured due to dry deposition.

The second possible source of error is related to the physical nature of snow and its melting characteristics. It is obvious that snow melt leads to water permeating the snowpack, leaching of heavy metal deposition from the surface may then occur. In this study melting had not affected the snow to any degree.

8. Conclusions

This paper documents the results obtained using a simple, cheap and effective method of dustfall collection. The main conclusions are:

(a) The secondary copper smelter at the centre of this study has proved to be a major source of metal fallout to the local area.

(b) Levels of metal deposition are elevated up to 50 times greater than the typical background level of sites not affected by copper refinery fallout.

(c) The addition of metals to the soil by deposition is also high enough to merit considerable concern; close to the works very high deposition of zinc would give a level of 4 times the DoE guideline.

(d) The spatial distribution of the fallout zones indicates that different source processes lead to different plumes. The particular problems caused by a possible bag filter fire for example are traced in this study as a trail of very heavy deposition.

(e) The snow surface technique has obvious limitations for use in this country where suitable snow conditions occur infrequently. When the opportunity presents itself this technique could be extremely useful, particularly around large sources of metal emission, for mapping to fine resolution the deposition levels.

(f) The technique not only gives benefits in the sense of easily interpreted results of good resolution but also has more practible advantage such as low cost, easy collection, simple analytical methods and sample system not prone to mechanical defects or vandalism.

APPENDIX D

The results of the deposition monitoring exercise in Walsall during Nov-Dec 1982.

This appendix contains the results of the main deposition monitoring exercise (Survey 1). The appendix also contains information on the statistical distirbutions of the survey results and the correlations between the seperate elements.

Contents

TABLE D 1

DEPOSITION RATES IN SQUARE 1,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	6.3	0.022	0.01	0.15	0.77	7.9	0.55	3.0	0.36	-1.0
2	4.7	0.019	0.04	0.13	0.61	12.4	0.76	3.0	0.40	10.2
3	7.4	0.030	0.08	0.08	0.85	18.5	1.67	4.9	0.71	99.7
4	5.6	0.019	0.04	0.06	0.76	28.5	0.65	3.4	0.54	15.3
5	3.9	0.026	0.03	0.22	0.48	23.6	0.77	3.2	0.61	9.4
6	4.7	0.027	0.03	0.22	1.19	25.0	1.42	5.2	0.07	12.9
7	12.1	0.023	0.04	0.38	4.78	34.1	0.42	7.9	1.50	21.0
8	7.1	0.025	0.01	0.15	1.12	25.5	0.96	3.9	0.68	-1.0
9	18.9	0.040	0.04	0.18	0.98	16.9	0.74	5.0	0.48	85.3

TABLE D 2

DEPOSITION RATES IN SQUARE 2,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	34.9	0.030	0.06	0.44	2.98	23.8	4.24	16.2	2.77	50.3
2	14.6	0.034	0.04	0.22	2.21	23.3	2.14	9.5	-1.00	9.5
3	16.7	0.040	0.04	0.17	2.21	19.7	2.31	7.6	1.77	108.3
4	13.1	0.032	0.06	0.19	2.21	19.1	2.00	6.1	1.73	43.2
5	16.0	0.030	0.04	0.23	1.85	18.7	2.37	8.2	1.54	83.2
6	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
7	8.8	0.030	0.05	0.44	2.50	22.8	2.37	4.2	1.73	80.2
8	14.9	0.045	0.07	0.22	4.34	14.9	1.91	6.7	1.71	44.7
9	4.4	0.037	0.04	0.12	1.72	8.7	1.34	3.7	0.65	12.2

MISSING VALUES INDICATED BY -1.0

TABLE D 3

DEPOSITION RATES IN SQUARE 3,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	20.0	0.079	0.06	0.44	8.84	22.7	3.44	6.4	3.29	83.8
2	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
3	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
4	5.5	0.022	0.02	0.06	2.13	6.0	1.10	3.9	0.82	8.8
5	14.1	0.041	0.11	3.55	6.19	123.0	9.70	8.3	2.23	98.1
6	9.5	0.039	0.05	0.10	2.49	6.3	0.88	5.0	0.58	79.9
7	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
8	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
9	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0

TABLE D 4

DEPOSITION RATES IN SQUARE 4,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	15.1	0.083	0.26	0.72	40.01	24.1	8.44	10.2	4.94	86.2
2	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
3	16.6	0.066	0.09	0.36	4.67	20.1	2.16	29.9	3.94	20.4
4	30.3	0.061	0.13	0.52	4.86	23.7	3.22	27.3	4.56	21.8
5	4.2	-1.000	0.08	0.37	2.00	14.3	0.78	8.5	1.03	12.6
6	28.1	0.048	0.09	0.28	3.38	107.0	2.75	15.4	3.12	17.0
7	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
8	23.9	0.063	0.13	0.36	5.65	25.9	2.78	29.0	5.10	27.5
9	12.8	0.050	0.09	0.36	5.57	25.3	3.71	26.4	2.38	22.1

MISSING VALUES INDICATED BY -1.0

TABLE D 5

DEPOSITION RATES IN SQUARE 5,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	5.7	0.020	0.04	0.07	3.29	8.2	1.13	4.0	0.46	46.1
2	9.7	0.027	0.04	0.03	6.66	14.9	2.21	8.3	1.21	68.8
3	10.5	0.074	0.10	0.63	7.22	17.6	2.16	6.6	1.07	68.2
4	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
5	-1.0	0.033	-1.00	-1.00	0.88	3.9	0.89	4.2	-1.00	-1.0
6	3.2	0.020	0.04	0.24	1.00	5.4	1.23	2.7	0.45	30.0
7	11.1	0.028	0.05	0.18	1.10	19.6	2.16	5.5	0.87	29.2
8	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
9	7.3	0.025	0.08	0.13	1.01	8.5	1.61	9.2	1.15	108.5

TABLE D 6

DEPOSITION RATES IN SQUARE 6,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	5.5	0.020	0.03	0.14	0.90	4.7	0.78	8.6	0.37	13.8
2	9.0	0.014	0.02	0.07	0.47	6.4	0.51	3.6	0.24	52.8
3	11.2	0.034	0.02	0.06	0.53	2.9	0.58	4.0	0.30	55.2
4	11.1	0.024	-1.00	0.07	0.36	4.0	0.17	4.3	0.31	67.5
5	5.4	0.022	0.01	0.04	0.21	4.1	0.36	3.1	0.31	64.9
6	5.0	0.018	0.03	0.10	0.83	7.3	1.67	3.9	0.53	70.9
7	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
8	4.0	0.033	0.05	0.12	0.53	7.2	1.12	3.2	0.34	3.1
9	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0

MISSING VALUES INDICATED BY -1.0

TABLE D 7

DEPOSITION RATES IN SQUARE 7,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	6.7	0.015	-1.00	0.25	0.39	28.6	7.22	4.7	1.29	-1.0
2	2.8	0.030	0.05	0.04	0.68	5.4	1.53	6.4	0.34	76.0
3	6.3	0.028	0.03	0.07	1.09	7.8	0.63	2.8	0.27	17.5
4	5.8	0.017	0.02	0.11	0.59	14.4	0.43	2.8	0.37	11.8
5	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
6	13.7	0.025	0.01	0.16	0.72	10.0	0.56	5.1	0.38	42.1
7	3.9	0.022	-1.00	0.09	0.29	5.4	0.65	2.8	0.30	7.5
8	2.8	0.020	0.02	0.05	0.23	4.5	0.03	-1.0	0.16	5.9
9	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0

TABLE D 8

DEPOSITION RATES IN SQUARE 8,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	8.3	0.015	-1.00	0.12	0.36	13.5	0.95	1.9	0.27	22.3
2	4.5	0.023	0.04	-1.00	0.31	5.7	0.46	2.8	0.19	18.3
3	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
4	7.4	0.019	0.04	0.10	0.81	8.3	0.61	5.0	0.27	13.4
5	5.3	0.039	0.03	-1.00	0.67	17.3	0.66	4.4	0.55	18.1
6	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
7	4.4	0.030	0.01	0.03	0.41	9.7	0.83	3.2	0.29	12.8
8	9.3	0.026	0.05	-1.00	0.36	23.2	0.25	6.7	0.54	4.4
9	6.8	0.018	0.03	0.09	0.70	22.8	-1.00	4.7	0.52	10.8

MISSING VALUES INDICATED BY -1.0

TABLE D 9

DEPOSITION RATES IN SQUARE 9,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	10.5	0.033	0.06	0.24	4.11	41.1	1.84	6.1	1.14	14.6
2	12.4	0.029	0.05	0.16	3.10	22.5	1.71	6.4	1.28	44.6
3	4.6	0.022	0.01	0.12	0.95	8.7	0.61	3.2	0.52	11.7
4	13.0	0.035	0.05	0.32	1.43	38.9	1.41	11.4	1.91	20.2
5	9.9	0.044	0.10	0.52	1.71	12.2	2.13	5.0	0.56	46.2
6	12.2	0.015	0.03	0.21	1.53	28.8	0.24	8.3	1.05	20.0
7	12.3	0.032	0.04	0.27	3.75	35.1	1.93	7.2	1.75	28.9
8	9.6	0.030	0.07	0.48	5.51	56.2	2.20	5.1	1.12	84.9
9	5.4	0.024	0.03	0.10	1.74	3.3	0.88	3.7	0.91	22.1

TABLE D 10

DEPOSITION RATES IN SQUARE 10,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	5.1	0.024	0.09	0.36	6.04	84.6	3.84	4.7	1.05	20.5
2	18.6	0.031	0.05	0.94	2.23	44.2	2.92	13.9	2.65	19.0
3	14.2	0.032	0.10	0.26	6.19	-1.0	2.75	9.9	1.67	46.8
4	9.5	0.030	0.17	0.30	31.50	36.8	4.02	0.7	1.35	64.9
5	6.4	-1.000	0.05	0.32	4.20	29.2	1.88	0.4	0.72	13.6
6	21.6	0.040	0.04	0.32	3.22	60.0	2.11	7.9	2.21	49.1
7	15.1	0.038	0.02	0.43	5.06	57.3	1.52	0.5	2.29	-1.0
8	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
9	22.9	0.041	0.64	0.31	4.18	104.3	1.64	10.9	4.47	40.2

MISSING VALUES INDICATED BY -1.0

TABLE D 11

DEPOSITION RATES IN SQUARE 11,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	25.1	0.072	0.10	0.48	9.17	40.0	51.43	10.5	3.28	389.5
2	7.0	0.040	0.10	0.16	7.07	17.0	2.74	4.7	0.97	22.6
3	2.9	0.034	0.07	0.20	1.06	10.1	1.18	3.6	0.69	12.1
4	16.9	0.055	0.24	0.41	3.66	22.0	3.78	8.6	2.61	33.2
5	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
6	10.0	0.038	0.04	0.32	3.63	15.6	2.01	6.7	1.16	148.6
7	11.2	0.035	0.06	0.12	1.32	11.0	1.67	5.0	0.64	53.5
8	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
9	13.4	0.046	0.05	0.28	1.71	12.4	2.14	9.3	1.66	106.5

TABLE D 12

DEPOSITION RATES IN SQUARE 12,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	11.2	0.063	0.09	0.29	9.29	31.7	3.24	10.2	1.47	53.1
2	17.1	0.074	0.16	0.38	68.66	28.5	28.49	10.2	2.52	85.6
3	15.9	0.062	0.09	0.41	7.71	30.3	3.64	17.1	2.02	33.8
4	10.4	0.055	0.12	0.40	10.97	20.0	2.88	13.6	1.30	15.5
5	22.6	0.056	0.04	0.27	5.41	39.4	2.44	9.4	3.16	18.8
6	14.2	-1.000	0.11	0.39	13.14	21.0	4.72	6.0	1.57	23.8
7	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
8	18.8	0.048	0.10	0.39	5.56	28.4	2.90	11.1	1.73	28.1
9	17.3	0.056	0.14	0.51	12.88	76.0	7.43	1.6	2.49	28.8

MISSING VALUES INDICATED BY -1.0

TABLE D 13

DEPOSITION RATES IN SQUARE 13,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	4.2	0.019	0.08	0.01	1.58	3.2	0.97	2.7	0.28	44.4
2	11.7	0.048	0.09	0.43	4.48	14.3	3.19	8.5	1.27	25.6
3	3.3	0.039	0.10	-1.00	2.25	3.2	1.53	10.2	0.67	1.6
4	47.3	0.052	0.18	0.45	14.37	13.2	4.87	10.2	2.47	51.1
5	18.4	0.064	0.13	0.22	4.51	28.5	3.24	7.7	1.80	25.3
6	26.2	0.044	0.12	0.41	3.16	71.7	2.46	11.1	2.68	25.9
7	21.2	0.044	0.11	0.33	3.39	19.5	3.22	11.1	2.42	54.7
8	5.0	-1.000	0.10	0.05	2.16	8.9	1.87	4.4	0.76	27.8
9	21.7	0.059	0.11	0.30	9.29	16.4	3.58	9.4	2.26	64.3

TABLE D 14

DEPOSITION RATES IN SQUARE 14,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
2	10.3	0.029	0.03	0.13	2.24	12.5	2.68	9.2	1.02	66.3
3	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
4	11.7	0.046	0.05	0.13	3.16	13.8	3.24	11.0	1.38	61.5
5	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
6	9.5	0.039	0.05	0.10	2.49	6.3	0.88	5.0	0.58	78.9
7	6.7	0.054	0.04	0.22	2.41	15.1	1.18	18.4	1.18	7.8
8	4.2	0.045	0.04	0.01	2.81	17.8	1.42	10.6	2.05	32.3
9	6.6	0.018	0.04	0.15	1.04	3.3	1.33	3.4	0.33	2.5

MISSING VALUES INDICATED BY -1.0

TABLE D 15

DEPOSITION RATES IN SQUARE 15,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	4.0	0.037	0.04	0.17	1.45	7.1	2.52	3.7	0.97	12.8
2	8.0	0.037	0.03	0.01	1.10	7.8	1.09	4.8	0.50	44.8
3	3.2	0.023	0.03	0.07	1.38	15.0	1.10	3.0	0.99	6.6
4	15.8	0.043	0.03	0.10	1.76	21.2	1.32	13.3	2.27	31.2
5	9.9	0.037	-1.00	0.11	0.82	19.1	2.62	3.9	2.48	13.7
6	8.3	-1.000	0.07	0.31	3.50	29.8	3.21	5.0	1.90	10.0
7	5.0	0.024	0.04	0.09	1.69	11.0	1.73	3.8	0.80	12.4
8	9.0	0.039	0.01	0.44	1.75	8.2	0.95	3.9	0.47	47.6
9	4.0	0.023	0.03	0.15	2.46	13.1	1.55	4.5	1.18	5.7

TABLE D 16

DEPOSITION RATES IN SQUARE 16,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	8.1	0.023	0.03	0.07	0.66	8.2	0.79	3.5	0.41	-1.0
2	4.3	0.013	0.02	0.44	0.72	11.7	1.09	3.3	0.45	9.6
3	16.0	0.046	0.08	0.84	4.76	183.8	5.98	1.7	7.61	142.6
4	4.4	0.022	-1.00	0.10	0.47	21.6	0.06	1.2	0.22	7.1
5	8.1	0.024	0.02	0.07	0.74	18.3	0.86	3.4	0.77	-1.0
6	6.0	0.031	0.03	0.41	1.07	37.0	1.01	4.5	1.37	21.1
7	16.7	0.036	0.03	0.31	2.17	42.9	1.74	7.0	1.46	34.4
8	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
9	2.4	0.013	-1.00	0.19	0.56	11.3	-1.00	2.6	0.42	92.6

MISSING VALUES INDICATED BY -1.0

TABLE D 17

DEPOSITION RATES IN SQUARE 17,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	14.1	0.028	0.05	0.07	1.95	19.3	2.28	10.1	1.31	6.9
2	26.4	0.030	0.04	0.45	1.99	27.5	1.63	18.4	2.27	5.7
3	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
4	15.4	0.030	0.03	0.22	1.98	19.2	2.22	11.0	1.57	24.1
5	17.0	0.022	0.04	0.15	1.38	19.7	3.00	9.2	1.83	8.6
6	7.3	0.025	0.08	0.13	1.86	8.5	2.11	9.2	1.15	108.5
7	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
8	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
9	16.9	0.045	0.08	0.28	-1.00	16.7	-1.00	9.2	1.82	105.1

TABLE D 18

DEPOSITION RATES IN SQUARE 18,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	3.0	0.025	0.03	-1.00	0.31	7.1	0.47	2.7	0.25	7.5
2	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
3	5.5	0.026	0.04	0.11	1.14	32.5	1.20	3.3	0.18	15.7
4	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
5	6.9	0.032	0.03	0.21	0.94	19.4	0.70	4.1	0.74	55.8
6	7.4	0.022	-1.00	0.10	0.74	10.4	0.53	6.7	0.40	51.5
7	6.2	0.056	0.03	0.21	0.71	13.5	1.47	3.0	3.03	7.9
8	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
9	3.7	0.031	0.02	-1.00	0.66	10.8	1.04	3.7	0.35	102.1

MISSING VALUES INDICATED BY -1.0

TABLE D 19

DEPOSITION RATES IN SQUARE 19,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	11.2	0.064	0.04	2.40	1.91	98.1	8.12	8.6	3.16	47.3
2	10.7	-1.000	0.03	0.09	1.41	92.9	1.52	11.4	2.62	42.6
3	10.7	0.064	-1.00	0.14	1.46	15.7	0.97	6.2	0.78	46.3
4	4.9	0.024	0.01	0.10	-1.00	-1.0	0.47	-1.0	0.05	68.9
5	5.2	0.018	0.02	-1.00	0.67	44.9	0.95	3.8	0.44	9.2
6	11.2	0.014	0.03	0.19	1.10	63.9	1.52	7.6	0.96	20.0
7	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
8	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
9	8.0	0.031	0.05	0.06	0.71	7.3	0.93	4.3	0.30	14.9

TABLE D 20

DEPOSITION RATES IN SQUARE 20,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	3.4	0.028	0.09	0.08	0.47	32.9	0.99	3.2	0.53	10.9
2	4.4	0.027	0.03	0.15	0.90	11.0	0.66	3.7	0.59	11.3
3	7.2	0.025	0.03	0.39	1.66	34.2	0.23	2.2	1.63	15.1
4	6.8	0.025	0.03	-1.00	1.09	5.7	0.65	3.2	0.32	15.6
5	9.5	0.026	0.02	0.20	0.64	12.1	0.44	-1.0	0.38	88.4
6	11.2	0.025	0.03	0.31	0.29	22.9	0.72	5.9	0.43	41.0
7	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
8	3.8	0.028	-1.00	0.30	0.38	7.0	0.70	3.1	0.28	15.0
9	6.7	0.026	0.09	-1.00	1.35	19.5	0.69	4.1	0.72	14.3

MISSING VALUES INDICATED BY -1.0

TABLE D 21

DEPOSITION RATES IN SQUARE 21,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	6.5	0.026	0.04	0.07	0.59	24.2	1.22	2.7	0.53	22.2
2	15.8	0.025	0.05	0.17	0.86	6.9	1.63	6.5	0.32	80.1
3	12.3	0.017	0.09	0.18	1.35	12.4	2.54	7.6	0.80	125.2
4	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
5	10.5	0.043	0.10	0.09	2.17	59.7	3.16	6.7	1.06	83.2
6	8.3	0.027	0.09	0.10	2.50	21.2	2.46	7.6	0.69	93.7
7	7.3	0.024	0.07	0.10	1.17	24.4	1.83	6.7	0.72	65.2
8	34.5	0.054	0.13	0.29	0.75	66.7	4.63	17.1	10.86	96.8
9	3.1	0.030	0.05	0.02	0.45	13.8	0.91	2.6	0.23	51.1

TABLE D 22

DEPOSITION RATES IN SQUARE 22,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	14.3	0.025	0.03	-1.00	2.16	41.7	1.47	5.1	1.13	84.4
2	3.9	0.025	0.02	0.13	0.79	8.0	0.47	2.9	0.44	12.1
3	4.2	0.016	0.03	0.11	0.40	9.9	0.62	2.9	0.26	8.5
4	5.5	0.027	0.08	0.17	1.00	8.6	1.12	3.9	0.48	15.8
5	1.8	0.026	-1.00	0.16	0.36	6.5	0.78	2.8	0.26	3.2
6	6.0	0.027	0.09	0.14	6.23	6.6	1.16	3.7	0.37	12.2
7	4.4	0.026	0.03	0.11	1.40	15.1	1.27	3.2	0.40	12.0
8	10.7	0.026	0.04	0.11	0.04	13.1	0.55	5.2	0.45	44.9
9	7.3	0.031	0.03	0.14	0.53	22.2	0.47	3.9	0.43	33.8

MISSING VALUES INDICATED BY -1.0

TABLE D 23

DEPOSITION RATES IN SQUARE 23,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	5.9	0.029	0.42	-1.00	0.51	9.1	0.64	3.5	0.43	17.6
2	5.2	0.023	0.01	-1.00	1.07	3.9	0.40	3.4	0.27	20.9
3	3.4	0.027	-1.00	0.04	-1.00	19.9	-1.00	10.1	0.76	5.3
4	5.6	0.017	0.02	0.06	0.51	64.6	1.52	3.9	0.60	11.3
5	5.9	0.016	0.03	0.06	0.16	8.1	0.60	3.3	0.20	14.8
6	4.0	0.015	-1.00	0.04	0.28	5.8	0.65	2.8	0.18	9.1
7	7.1	0.032	0.04	0.06	0.21	31.4	0.65	3.5	0.74	13.5
8	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
9	5.1	0.023	0.02	-1.00	0.32	3.1	0.80	2.9	0.27	30.0

TABLE D 24

DEPOSITION RATES IN SQUARE 24,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	6.2	-1.000	-1.00	0.04	2.94	8.0	1.52	3.5	-1.00	-1.0
2	4.4	0.049	0.14	0.11	3.65	8.4	5.17	3.8	0.30	39.0
3	5.3	-1.000	0.08	0.04	1.60	7.6	1.83	2.7	0.20	69.4
4	10.2	0.036	0.27	0.38	5.73	27.8	7.84	4.9	0.60	115.5
5	6.1	0.010	0.10	0.02	2.44	18.7	2.55	3.5	0.50	74.4
6	5.5	0.032	0.06	-1.00	1.61	19.8	1.96	3.8	0.54	39.6
7	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
8	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
9	9.5	0.022	0.06	0.12	4.61	9.4	2.08	2.9	0.36	28.5

MISSING VALUES INDICATED BY -1.0

TABLE D 25

DEPOSITION RATES IN SQUARE 25,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	16.1	0.030	0.03	0.59	1.41	144.0	2.73	11.0	11.40	26.0
2	6.5	0.030	0.09	0.12	0.57	11.1	1.55	4.2	2.17	12.8
3	5.8	0.026	0.08	0.06	0.57	11.4	0.90	2.8	0.51	12.3
4	13.9	0.019	-1.00	0.11	0.70	2.2	0.82	7.4	1.06	46.0
5	9.0	0.023	0.06	0.13	0.92	15.2	1.81	4.5	1.65	27.5
6	6.4	0.032	0.01	0.06	1.38	10.3	1.81	2.0	0.46	12.4
7	6.8	0.026	0.05	0.11	0.47	12.2	0.54	9.7	0.38	14.7
8	10.8	-1.000	0.03	0.12	0.34	12.8	0.86	4.0	0.51	29.2
9	4.3	0.016	0.03	0.14	0.29	21.0	1.60	3.4	0.57	5.6

TABLE D 26

DEPOSITION RATES IN SQUARE 26,(mg/m^2/30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	3.5	0.027	0.11	-1.00	0.95	14.7	1.68	3.8	0.37	10.6
2	4.9	0.030	0.06	0.03	0.59	8.5	0.95	3.6	0.32	9.0
3	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
4	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
5	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
6	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
7	7.8	0.026	0.09	0.05	0.52	1.4	0.55	3.4	0.14	54.6
8	4.5	0.024	0.10	0.31	1.52	22.4	1.42	3.6	0.85	33.4
9	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0

MISSING VALUES INDICATED BY -1.0

TABLE D 27

DEPOSITION RATES IN SQUARE 27,(mg/m /30d)

	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
1	9.0	0.029	0.08	0.01	0.74	4.9	0.49	4.3	0.19	40.8
2	9.1	0.031	0.08	-1.00	1.19	6.0	1.14	8.1	0.39	41.9
3	6.1	0.019	0.10	0.19	0.68	2.6	1.29	4.1	0.27	13.7
4	11.1	0.022	0.07	0.12	0.40	2.8	1.16	4.7	0.21	51.0
5	-1.0	-1.000	-1.00	-1.00	-1.00	-1.0	-1.00	-1.0	-1.00	-1.0
6	9.6	0.014	0.05	0.08	0.40	2.0	0.66	3.9	0.19	37.0
7	16.0	0.033	0.09	0.15	1.22	23.7	1.41	6.2	1.15	15.8
8	7.6	0.062	0.04	0.26	0.81	4.1	0.54	4.3	0.25	32.8
9	4.0	0.033	0.10	0.26	0.89	7.6	1.25	15.9	1.11	36.4

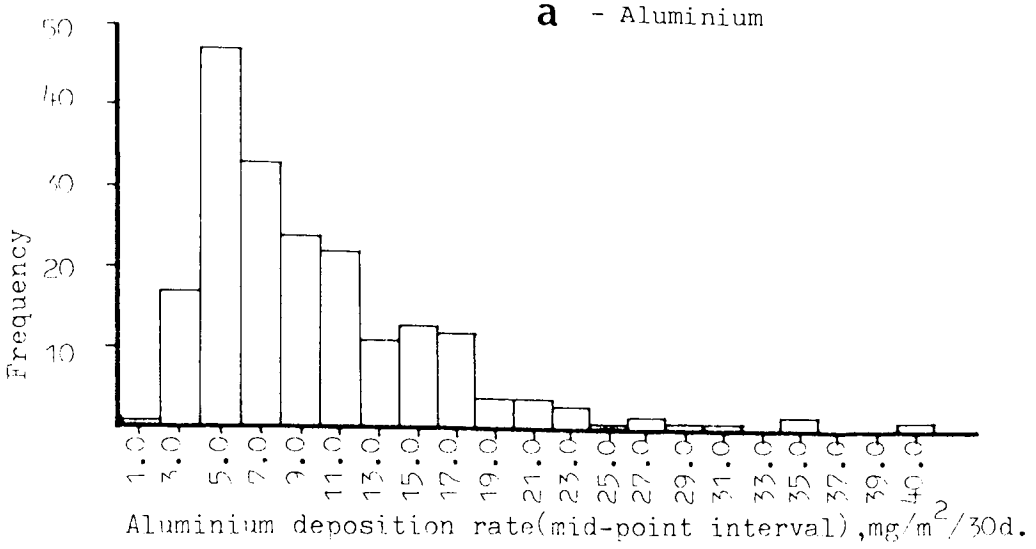
MISSING VALUES INDICATED BY -1.0

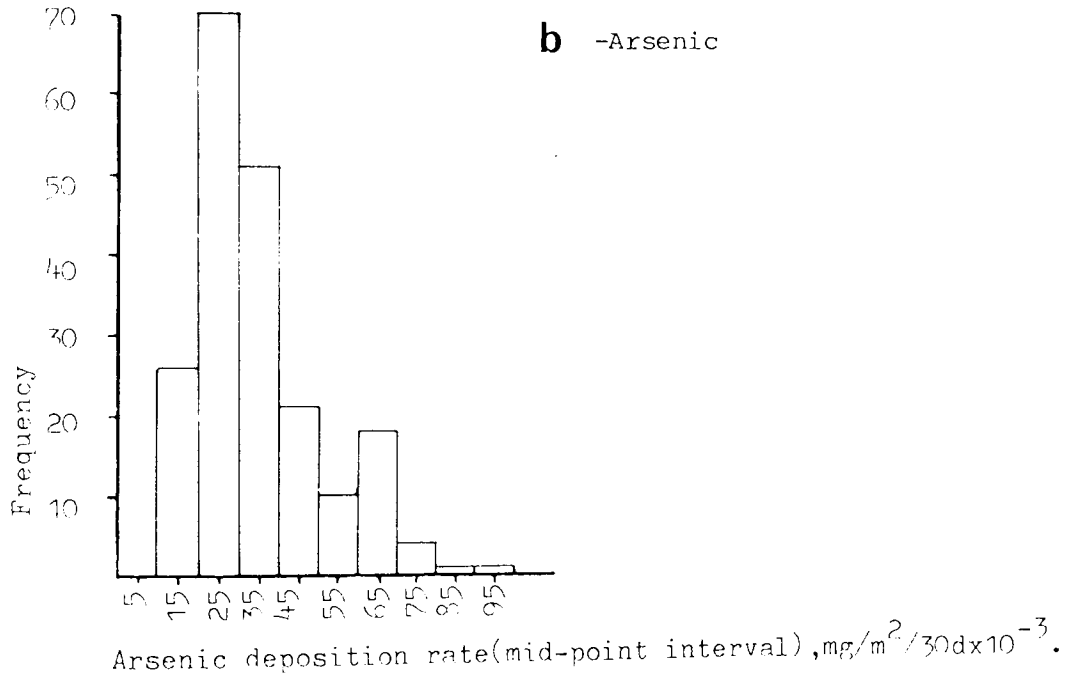
	Al	As	Cd	Cr	Cu	Fe	Pb	Mg	Mn	Zn
Aluminium	1.00	0.49	0.31	0.28	0.28	0.38	0.32	0.60	0.63	0.30
Arsenic		1.00	0.34	0.34	0.47	0.24	0.42	0.48	0.49	0.26
Cadmium			1.00	0.17	0.34	0.22	0.22	0.22	0.29	0.13
Chromium				1.00	0.19	0.54	0.29	0.21	0.35	0.21
Copper					1.00	0.14	0.52	0.17	0.25	0.21
Iron						1.00	0.23	0.19	0.66	0.15
Lead							1.00	0.18	0.29	0.66
Magnesium								1.00	0.53	0.09
Manganese									1.00	0.21
Zinc										1.00

TABLE D28 Matrix of correlation coeffients r for survey 1

--- p 0.05

___ p 0.01





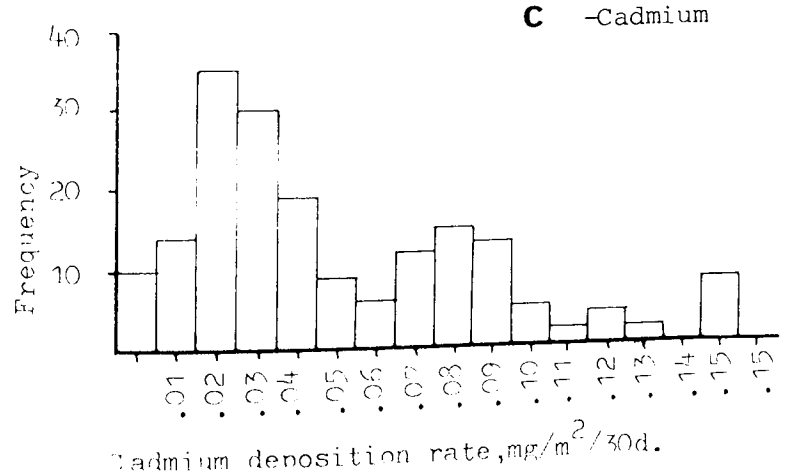
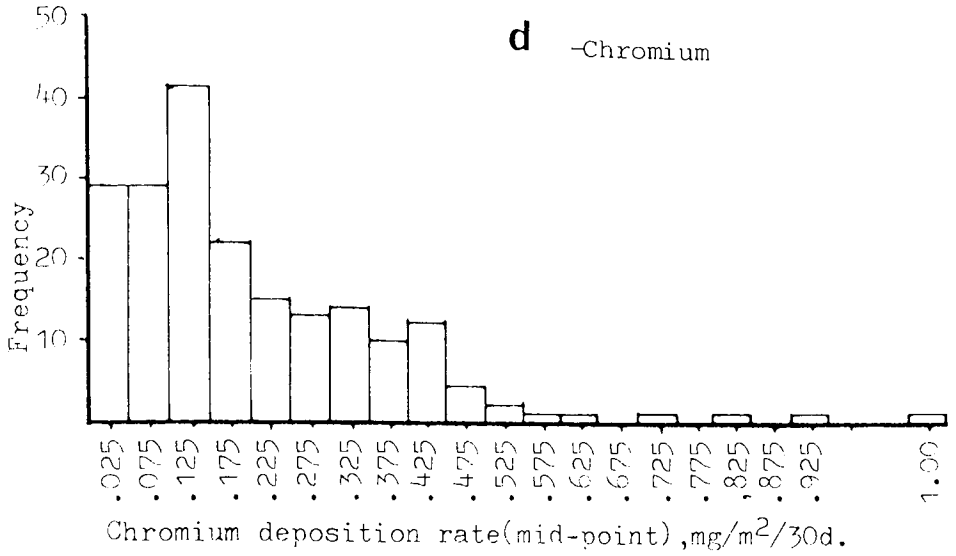
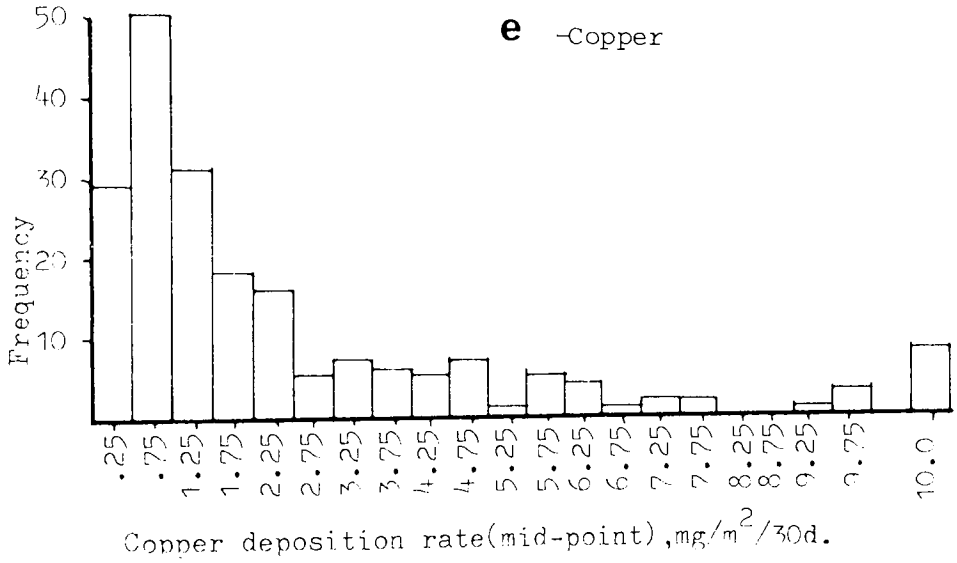
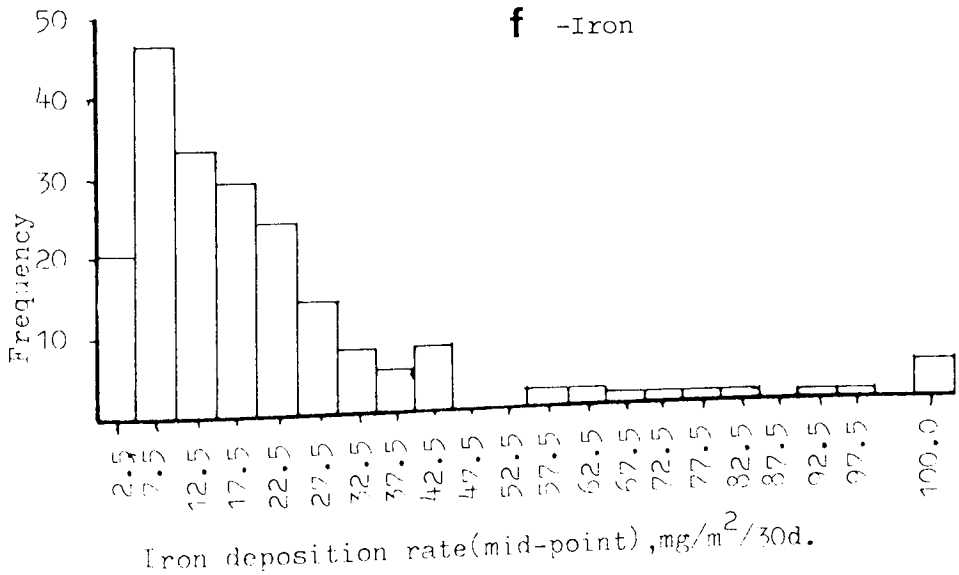
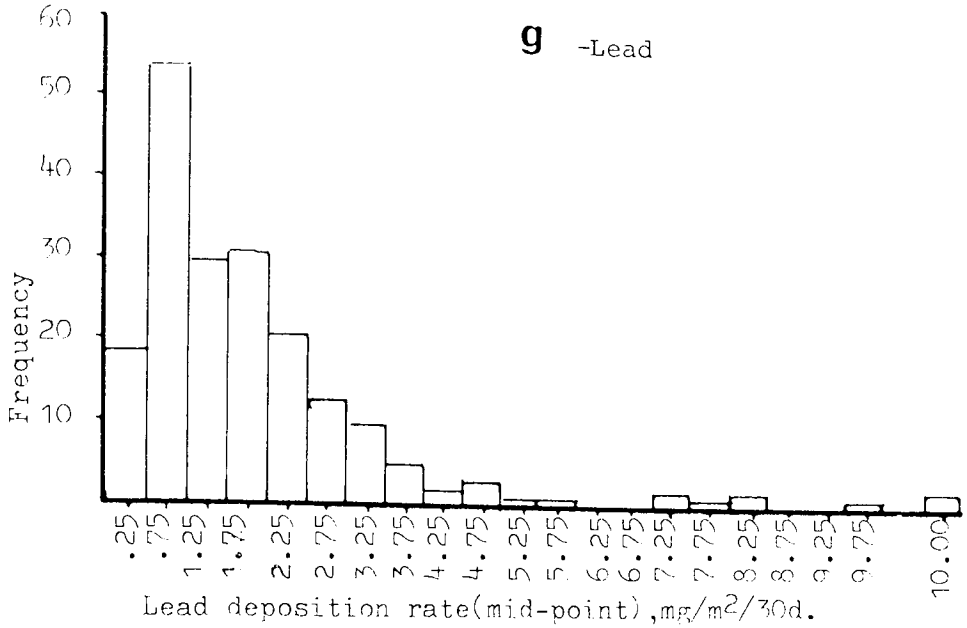


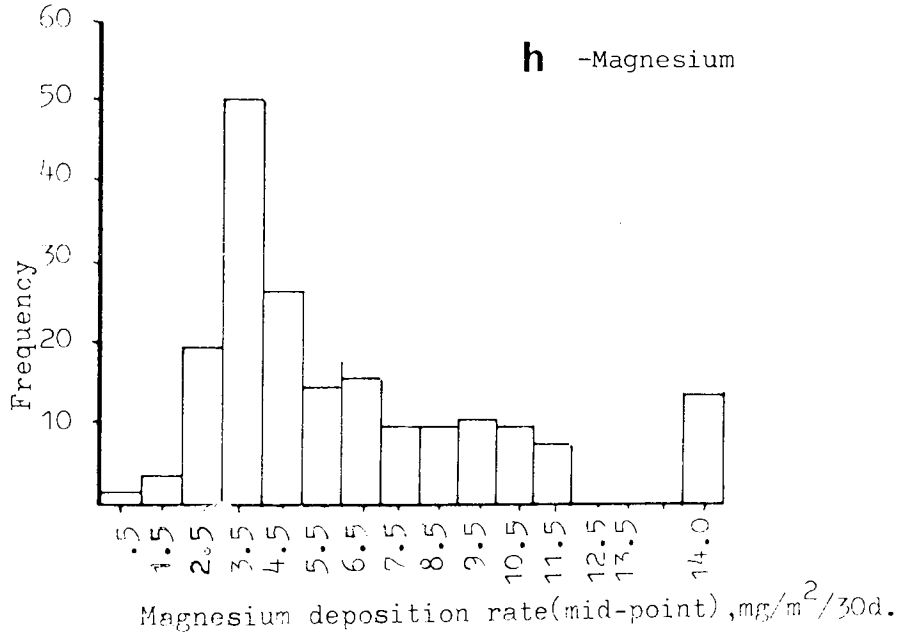
FIGURE D1 (a)-(j) FREQUENCY DISTRIBUTIONS FOR THE TEN SURVEY METALS IN SURVEY 1.

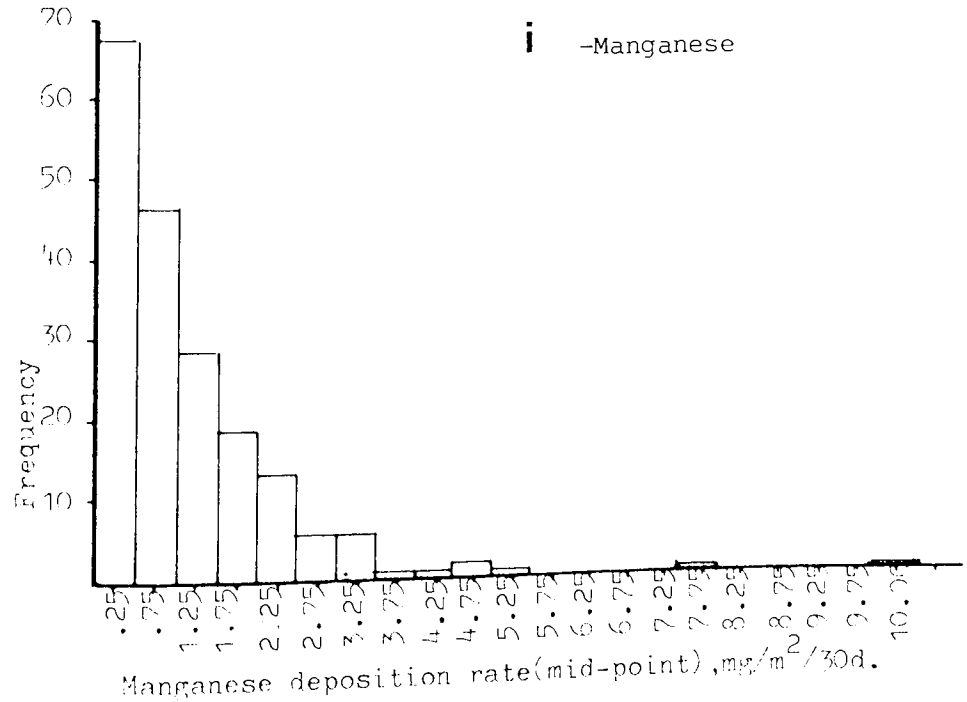

d -Chromium
Frequency
50
40
30
20
10
.025
.075
.125
.175
.225
.275
.325
.375
.425
.475
.525
.575
.625
.675
.725
.775
.825
.875
.925
1.00
Chromium deposition rate(mid-point),mg/m2/30d.

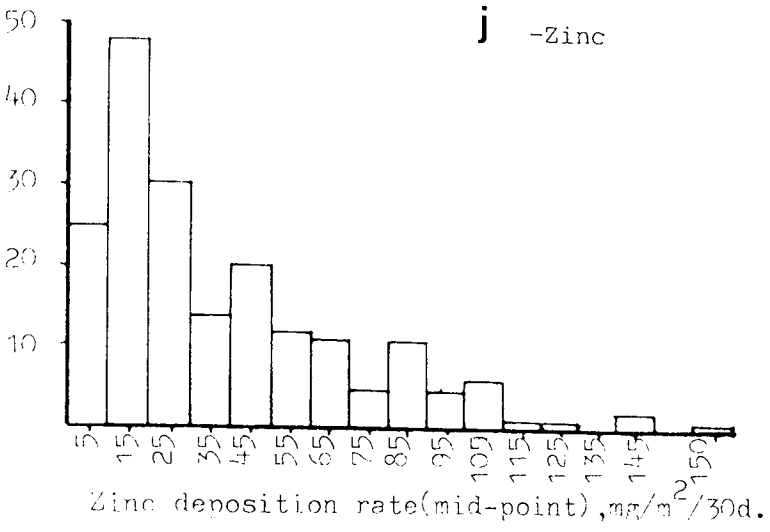

e -Copper
Frequency
50
40
30
20
10
.25
.75
1.25
1.75
2.25
2.75
3.25
3.75
4.25
4.75
5.25
5.75
6.25
6.75
7.25
7.75
8.25
8.75
9.25
9.75
10.0
Copper deposition rate(mid-point),mg/m2/30d.


f -Iron
Frequency
50
40
30
20
10
2.5
7.5
12.5
17.5
22.5
27.5
32.5
37.5
42.5
47.5
52.5
57.5
62.5
67.5
72.5
77.5
82.5
87.5
92.5
97.5
100.0
Iron deposition rate(mid-point),mg/m2/30d.


g -Lead
Frequency
60
50
40
30
20
10
.25
.75
1.25
1.75
2.25
2.75
3.25
3.75
4.25
4.75
5.25
5.75
6.25
6.75
7.25
7.75
8.25
8.75
9.25
9.75
10.00
Lead deposition rate(mid-point),mg/m2/30d.


h -Magnesium
Frequency
60
50
40
30
20
10
.5
1.5
2.5
3.5
4.5
5.5
6.5
7.5
8.5
9.5
10.5
11.5
12.5
13.5
14.0
Magnesium deposition rate(mid-point),mg/m2/30d.


i -Manganese
Frequency
70
60
50
40
30
20
10
.25
.75
1.25
1.75
2.25
2.75
3.25
3.75
4.25
4.75
5.25
5.75
6.25
6.75
7.25
7.75
8.25
8.75
9.25
9.75
10.25
Manganese deposition rate(mid-point),mg/m2/30d.


j -Zinc
50
40
30
20
10
5
15
25
35
45
55
65
75
85
95
105
115
125
135
145
150
Zinc deposition rate(mid-point),mg/m²/30d.

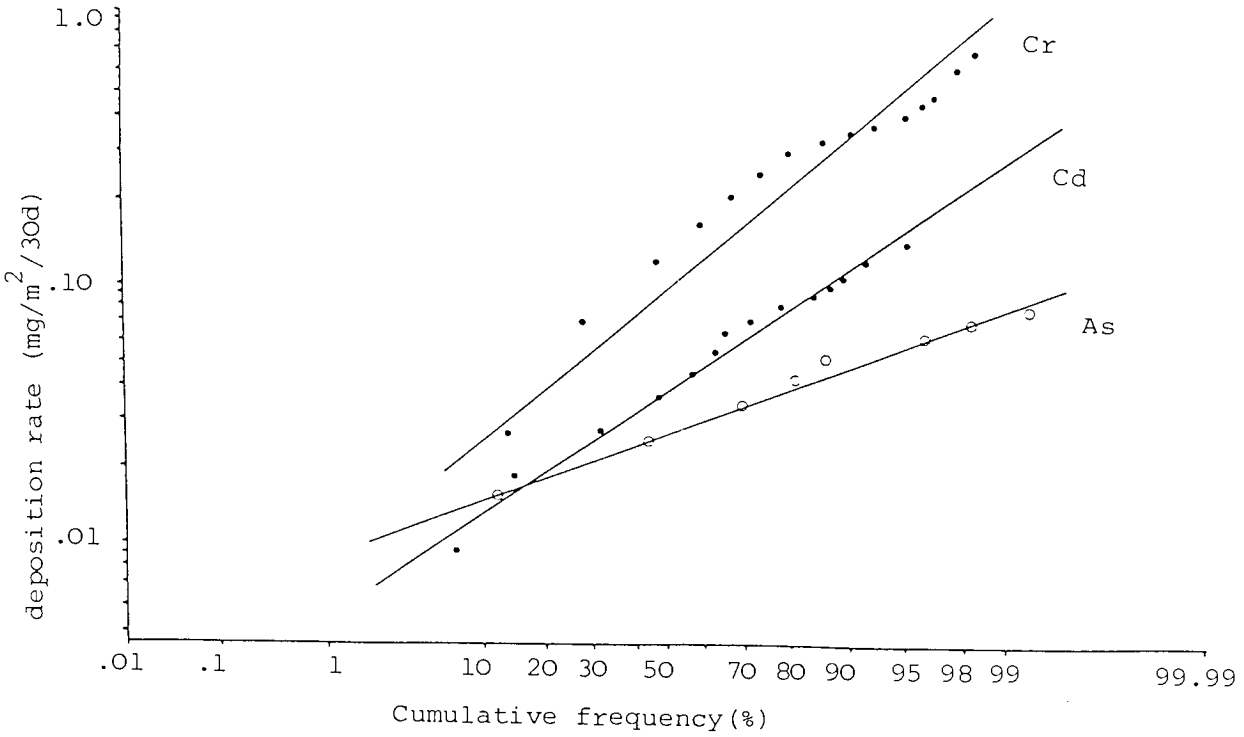


FIGURE D2 Log-probability plots for As,Cd and Cr.

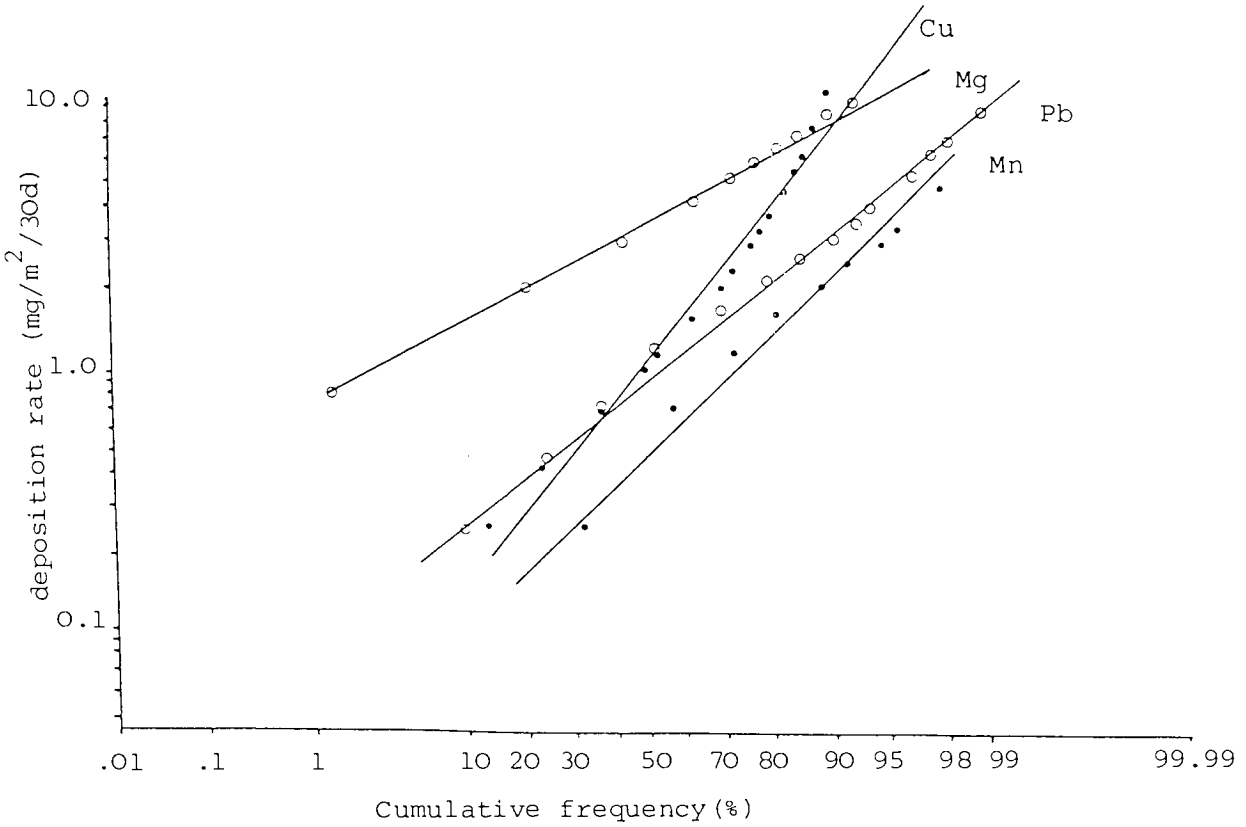


FIGURE D3 Log-probabilty plots for Cu,Pb,Mg and Mn.

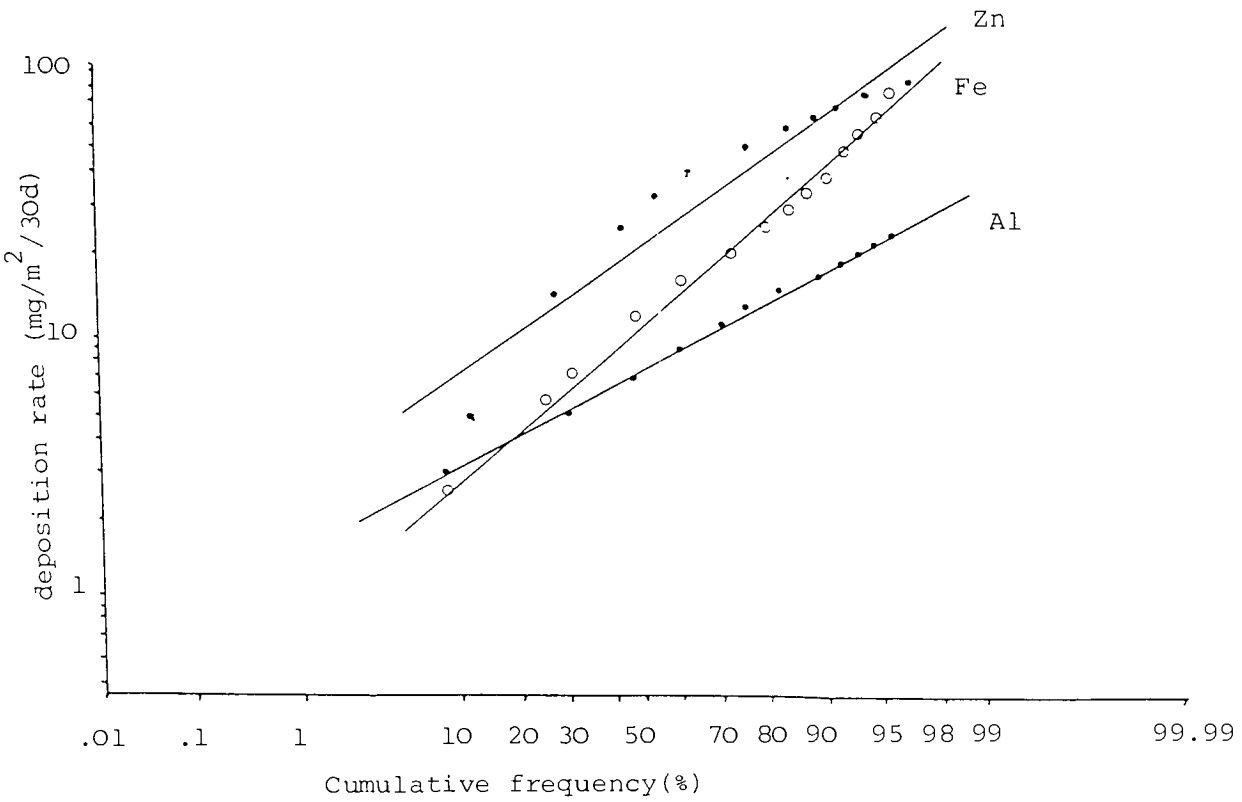


FIGURE D4 Log-probability plots for Al,Fe and Zn.

APPENDIX E

Listing of the Fortran computer program that was used to calibrate the source-based deposition model described in section 7.4.

```
C DEPOSITION MODEL          USES SIMPLE PARAMETERS OF SOURCE LOCATION TO
C                           PREDICT LEVELS OF DEPOSITION AT RECEPTORS
C
C S.A.SIMMONS
C UNIVERSITY OF ASTON  1983
C
C
      CALL DISTIN
      STOP
      END
C
C SUBROUTINE DISTIN
C
C
C  COMPUTES ALL DISTANCES,ANGLES AND SEGMENTS FOR SOURCES TO RECEPTORS
C THEN APPLIES PREDICTION MODEL OF THE FORM -
C
C       DEPOSITION = F(WIND SPEED).F(DISTANCE).(EMISSION)
C
C  THIS IS THEN WEIGHTED FOR WIND DIRECTION FREQUENCY
C
C
      SUBROUTINE DISTIN
      DIMENSION ALATS(15),ALONGS(15)
      DIMENSION ALATF(22),ALONGF(22),SOURCE(22)
      DIMENSION DATA(15,15)
       REAL N,NE,NW
       NS=21
C     INITIALIZE ANALYTICAL CONSTANTS
        A=0.347
        B=0.05
        C=0.375
C N TO NW ARE WIND DIRECTION FREQUENCIES
        N=.04
        NE=.04
        E=.06
        SE=.05
        S=.11
        SW=.27
        W=.30
        NW=.13
C  SPEED TO SPEED8 ARE THE MEAN WIND VELOCITIES FOR EACH WIND SEGMENT
        SPEED=10.0
        SPEED1=8.3
        SPEED2=3.7
        SPEED3=4.0
        SPEED4=6.9
        SPEED5=17.6
        SPEED6=17.1
        SPEED7=15.9
        SPEED8=10.5
      DO 20 J=1,NS
      READ(12,40)ALATF(J),ALONGF(J),X
   20 SOURCE(J)=X
   40 FORMAT(2X,2F4.0,F5.1)
        SUM1=940
        DO 170 JL=1,15
        SUM2=940
```

```
            ALONGS(JL)=SUM1
            DO 169 JK=1,15
            ALATS(JK)=SUM2
            ADD=0.0
            SLONG=ALONGS(JL)
            SLONG=SLONG+1.0
            DO 168 JM=1,5
            SLAT=ALATS(JK)
            SLAT=SLAT+1.0
            DO 167 JN=1,5
            TCONC=0.0
           DO 151 JC=1,NS
              ELAT=ALATF(JC)
              ELONG=ALONGF(JC)
              ASQ=(SLAT-ELAT)**2
              BSQ=(SLONG-ELONG)**2
              DIST=(SQRT(ASQ+BSQ))/10
              IF (DIST.GT.4.7)GO TO 151
              FREQ=0.0
C
               TLAT=ELAT-SLAT
               TLONG=ELONG-SLONG
               IF(TLAT.GT.0.0.AND.TLONG.GT.-0.0009)GO TO 105
               IF(TLAT.GT.0.AND.TLONG.LT.0)GO TO 110
               IF(TLAT.LT.0.0009.AND.TLONG.LT.-0.0009)GO TO 120
               IF(TLAT.LT.0.0.AND.TLONG.GT.-0.0009)GO TO 100
C
C            I
C            I
C       4    I    1
C            I
C   ---------I-------- X
C            I
C       3    I    2
C            I
C            I
C            Y
C
C-------------------------------------------------------------------
C CASE 4- LAT LT 0  LONG GT 0
C
  100             IF(TLONG.LT.0.0009.AND.TLAT.GT.-0.0009)GO TO 106
                  IF(TLONG.LT.0.0009)GO TO 90
                  THETA=360+ATAN (TLAT/TLONG)*57.29
                  GO TO 95
   90             THETA=270.0
   95             GO TO 130
C-------------------------------------------------------------------
C CASE 1- LAT AND LONG POSITIVE
C
  105             IF(TLONG.LT.0.0009.AND.TLAT.LT.0.0009)GO TO 106
                  IF (TLONG.LT.0.0009)GO TO 107
                  THETA=ATAN(TLAT/TLONG)*57.29
                  GO TO 109
  106             THETA=0.0
                  GO TO 109
  107             THETA=90
  109             GO TO 130
```

```
C-----------------------------------------------------------------------
C CASE 2- LAT GT 0  LONG LT 0
C
  110                IF (TLAT.LT.0.0009.AND.TLONG.LT.0.0009)GO TO 106
                    THETA=180+ATAN(TLAT/TLONG)*57.29
                   GO TO 130
C-----------------------------------------------------------------------
C CASE 3- LAT AND LONG NEGATIVE
C
  120            IF(TLONG.GT.-0.0009.AND.TLONG.LT.0.0009)GO TO 122
                THETA=180+ATAN(TLAT/TLONG)*57.29
               GO TO 130
  122             THETA=180.0
  130              IF(THETA.LT.0.000001)GO TO 140
                   IF (THETA.LT.22.5)GO TO 141
                   IF (THETA.LT.67.5)GO TO 142
                   IF (THETA.LT.112.5)GO TO 143
                   IF (THETA.LT.157.5)GO TO 144
                   IF (THETA.LT.202.5)GO TO 145
                   IF (THETA.LT.247.5)GO TO 146
                   IF (THETA.LT.292.5)GO TO 147
                   IF (THETA.LT.337.5)GO TO 148
                   GO TO 141
  140              FREQ=1.0
                   WS=SPEED
                   GO TO 149
  141              FREQ=N
                   WS=SPEED1
                   GO TO 149
  142              FREQ=NE
                   WS=SPEED2
                   GO TO 149
  143              FREQ=E
                   WS=SPEED3
                   GO TO 149
  144              FREQ=SE
                   WS=SPEED4
                   GO TO 149
  145              FREQ=S
                   WS=SPEED5
                   GO TO 149
  146              FREQ=SW
                   WS=SPEED6
                   GO TO 149
  147              FREQ=W
                   WS=SPEED7
                   GO TO 149
  148              FREQ=NW
                   WS=SPEED8
  149           CONC=FREQ*((1.0/WS)*(C-A*DIST**B)*SOURCE(JC))
                TCONC=TCONC+CONC
```

```
  151   CONTINUE
        ADD=ADD+TCONC
            SLAT=SLAT+2.0
  167   CONTINUE
          SLONG=SLONG+2.0
  168   CONTINUE
        ADD=(ADD/25.0)-1.0
        DATA(JK,JL)=ADD
        SUM2=SUM2+10.0
  169   CONTINUE
        SUM1=SUM1+10.0
  170   CONTINUE
       RETURN
       END
£VXECUTE
```

REFERENCES AND BIBLIOGRAPHY

Agricultural Development and Advisory Service (1971)
Permissable levels of toxic metals in sewage used on agricultural land.
M.A.F.F. Advisory Paper No.10.

Aitchison, J. and Brown, J.A.C. (1957)
The Lognormal Distribution.
Cambridge University Press.

Alpert, D.J. and Hopke, P.K. (1980)
A Quantitative determination of sources in the Boston Urban Aerosol.
Atmospheric Environment 14, 1137-1146

Alpert, D.J. and Hopke. P.K. (1981)
A determination of the sources of airborne particles collected during the Regional Air Pollution Study.
Atmospheric Environment 15, 675-687.

American National Standards Institute (1970)
Collection and Analysis of Dustfall (Settleable Particles).
ASTM D1739-70

Anderson, A. Hovmand, M.F. and Johnsen, I. (1978)
Atmospheric heavy metal deposition in the Copenhagen area.
Environmental Pollution B 17, 133-151

Atkins, M.H. and Lowe, J.F. (1979)
The Economics of Pollution Control in the Non-Ferrous Metals Industry.
Pergammon Press, Oxford.

Auwera, Van der (1977)
Forecasting the air pollution potential by means of a multiple regression model.
8th International Technical Meeting on Air Pollution Modelling and its applications.NATO.

Ball, D.J. and Bernard, R.E. (1978)
The Greater London Air Pollution Emission Inventory.
Atmospheric Environment 12, 975-978.

Barltrop, D. and Khoo, H.E. (1975)
The influence of nutritional factors on lead absorption.
Postgraduate Medical Journal, 51, 795-800.

Beaman, A.L. and Kingsbury, R. (1982)
Assessment of Nuisance from Deposited Particles using a simple and inexpensive measuring System.
Clean Air, 11, 77-81.

Beavington, F. (1975)
Heavy Metal contamination of vegetables and soil in domestic gardens around a smelting complex
Environmental Pollution, 9, 211-217.

Beavington, F. (1977)
Trace elements in rainwater and dry deposition around a smelting complex.
Environmental Pollution, 13, 127-131.

Benkowitz, C.M. (1982)
Compilation of an inventory of anthropogenic emissions in the United States and Canada.
Atmospheric Environment, 16, 1551-1563.

Bennett, R.L. and Knapp, K.T. (1982)
Characterisation of particulate emissions from wastewater sludge incinerators.
En vironmental Science and Technology, 16, 831-836.

Berkowitz, R. and Prahm, L.P. (1978)
Pseudospectral Simulation of dry deposition from a point source.
Atmospheric Environment, 12, 379-387.

Blifford, I.H. and Meeker, G.O. (1967)
A Factor Analysis model of large scale Pollution.
Atmospheric Environment 1, 147-157.

Bosanquet, C.H. (1950)
Dust deposition from chimney stacks.
Proceedings Institute of Mechanical Engineers, 162,355-367.

Boutron, C. (1979)
Past and present day tropospheric fallout fluxes of Pb, Cd, Cu, Zn and Ag in Antarctica and Greenland.
Geophysical Research Letters 6,159-162.

Boutron, C and Lorious, C. (1979)
Trace metals in Antarctic snow since 1914.
Nature 277, 551-554.

Bradley, J.P. Goodman, P. Chan, I.Y.T. and Buseck, P.R. (1981)
Structure and Evolution of Fugitive Particles from a Copper Smelter.
Environmental Science and Technology 15, 1208-1212.

British Standard 5497, (1979)
Precision of test methods;
Part I, Guide to the determination of repeatability and reproducibility of a standard test method.
British Standards Institution.

Brookfield, C. (1983)
Scrapyards and the recovery of metals from waste materials.
Proceedings of the National Society for Clean Air 50th Conference, Torquay.

Browning, E. (1961)
Toxicity of Industrial Metals.
Butterworths, London.

Bryce-Smith, D. and Stephens, R. (1980)
Lead or Health (2nd Edition).
Conservation Society Pollution
Working Party, London.

Buchauer (1973)
Contamination of soil and vegetation near a zinc
smelter by zinc, cadmium, copper and lead.
Environmental Science and Technology 7,131-135

Budiansky, S. (1980)
Dispersion Modelling.
Environmental Science and Technology 14,370-374.

Calder, K.L. (1977)
Multiple - source
Models of Urban Air Pollution ;
their general structure.
Atmospheric Environment 11, 403-414.

Carey, W.I. (1959)
Atmospheric deposits in Britain:
A study of dinginess.
International Journal of Air and Water
Pollution 2,1-26.

Cass, G.R. and McRae, G.J. (1983)
Source - Receptor Reconciliation of Routine
Air Monitoring Data for trace Metals; An
emission inventory Assisted Approach.
Environmental Science and Technology 17,129-139.

Caulcott, R. and Boddy, R. (1983)
Statistics for analytical chemists.
Chapman and Hall. London

Cawse, P.A. (1974)
A survey of atmospheric trace elements in
United Kingdon (1972-73).
A.E.R.E,R-7669

Cawse, P.A. (1977)
A survey of atmoshperic trace elements in
the United Kingdom.
A.E.R.E. R8869

Cawse, P.A. and Turner, G.J. (1981)
Trace elements in
vegetables from allotments in Walsall, 1979.
A.E.R.E. G1653.

Chamberlain, A.C. (1966)
Transport of lycopodium spores and other small
particles to rough surfaces. Proceedings of the
Royal Society A296,45-70.

Chatfield, C. (1978)
Statistics for technology.
Chapman and Hall, London.

Clayton, P. (1981)
The measurement of particulate and selected metal concentrations in the neighbourhood of a steelworks.
Warren Spring Laboratory Report, LR415 AP.

Clifford, A.A. (1973)
Multivariate Error Analysis
Applied Science Publishers Ltd, London.

Clough, W.S. (1975)
The deposition of particles to moss and grass surfaces.
Atmospheric Environment 9,1113-1119.

Clymo, R.S. (1963)
Ion exchange in Sphagnum and its relationship to bog ecology.
Annals of Botany 27,309-324.

Cochran, W.G. and Cox, C.M. (1957)
Experimental Designs.
2nd Edition, John Wiley and Sons.

Commission of the European Communities (1978)
Criteria (Dose/effect relationships) for cadmium.
Report EUR 5697 EEC, Luxembourg

Commission of the European Communities (1980)
Study into the emission of air pollutants coming from the use of coal within the United Kingdom.
National Coal Board, London.

Commission of the European Communities (1981)
Ecotoxicology of Cadmium
EUR 7499EN.

Committee on the Challenges of Modern Society (1978)
Air Pollution Emissions Inventory Systems.
NATO CCMS/N104.

Cooney, P.A. and Blake, P.G. (1982)
Lead in Paint: a major playground hazard.
Environmental Health, 90,3-5.

Cooper, J.A. and Watson, J.G. (1980)
Receptor orientated methods of air particulate source appointment.
Journal of the Air Pollution Control Association 30, 1116-1125.

Corbett, J.O. (1981)
The Validity of source-depletion and
alternative approximation methods for
a Gaussian Plume subject to dry deposition.
Atmospheric Environment 15, 1207-1213.

Core, J.E., Cooper, J.A., Hanrahan, P.L
and Cox, W.M. (1982)
Particulate Dispersion Model Evaluation.
A new approach using receptor models.
Journal of the Air Pollution Control Association 32,
1142-1147.

Core, J.E., Hanrahan, P.L. and Cooper, J.A. (1981)
Air particulate control strategy development:
A new approach using mass balance methods.
In Atmospheric Aerosols/Air Quality Relationships.
Ed. E.S Macias and P.K Hopke.
A.C.S Symposium, Nevada.

Corn, M. (1976)
In Air Pollution 3rd Edition Vol. 1
Ed A.C. Stern, Acedemic Press, New York.

Crossley, P and Hill, W.H. (1982)
Field comparison of the relative efficency
of two types of deposit gauge.
Clean Air 12, 91-98.

Crump, D.R. and Barlow, P.J. (1982)
Factors controlling the lead content of
pasture grass.
Environmental Pollution B3,181-192.

Crumpler, T.B. and Yoe, H.J. (1946)
Chemical Computation and Errors.
Wiley, New York.

Cunningham, J (1984)
International Standards Organisation,
London. Personnal Communication

Davidson, C.I,and Friedlander, S.K. (1978)
A filtration model for aerosol dry
deposition: application to trace metal
deposition from the atmosphere.
Journal of Geophysical Research 83, 2343-2352.

Davies, B.E. and Holmes P. L. (1982)
Lead contamination in roadside soils and grass
in Birmingham, England, in relation to
naturally occuring levels.
Journal of Agricultural Science, Cambridge 79, 479-484

Davies, B.E. and Roberts, L.J. (1975)
Heavy metal in soils and radish in a mineralised limestone area of Wales, Great Britain.
Science of the Total Environment 4, 249-261.

Davies, B.E., Conway, D. and Holt, S. (1979a)
Lead Pollution of London soils: a potential restriction on their use for growing vegetables.
Journal of Agricultural Science, Cambridge 93, 749-752.

Davies, B.E. and Ginnever, R.G. (1979b)
Trace metal contamination in soils and vegetables in Shipham, Somerset.
Journal of Agricultural Science, Cambridge 93,753-756.

Davies, W .E et al (1973)
Emission study of industrial sources of lead air pollutants, 1970.
NTIS, U.S. Department of Commerce PB 223-652.

Davies, B.J. anmd Clayton, P. (1974)
1) Assessment of ambient concentrations of heavy metals in the neighbourhood of James Bridge Copper Works (IMI Ltd).

2) Assessment of particle and heavy metal concentrations in the ambient atmosphere at a site close to Brookside Metals Ltd.

3) Assessment of ambient concentrations of heavy metals in the neighbourhood of Elkingtons Copper Refinery Ltd.
Confidential Reports, Warren Spring, Laboratory, Stevenage.

Department of the Environment (1974)
Monitoring of the Environment in the United Kingdom.
H.M.S.O. London.

——————————— (1976)
Enviromental Mercury and Man.
Pollution Paper No. 10, H.M.SO. London.

——————————— (1980)
Cadmium in the Environment and its significance to man.
Pollution Paper No. 17, H.M.S.O. London.

——————————— (1981a)
European Community Screening Programme for lead. United Kingdon results for 1979-1980.
Pollution Report No. 10. D.O.E. London.

——————————— (1981b)
Report of the Sub-Committee on the disposal of sewage sludge to land.
National Water Council Standing Technical Committee on the Disposal of Sewage Sludge. Report No.20.

———————————————— (1982a)
Blood-lead concentrations in pre-school children in Birmingham.
Pollution Report No. 15,D.O.E., London.

———————————————— (1982b)
Lead in the Environment
DOE circular No.22/82 H.M.S.O., London.

———————————————— (1983)
European Community Screening programme for lead: United Kingdom results for 1981.
Pollution Report No. 18. DOE, London.

DOE and the National Water Council (1977)
Report of the Working Party on the Disposal of sewage sludge to land.
DOE Standing Technical Committee Report No.5. H.M.S.O, London.

Department of Health and Social Security (1980)
Lead and Health: a report of a D.H.S.S Working Party on lead in the environment.
H.M.S.O, London.

Dorn, C.R. and Pierce, J.O. Chase, G.R. and Phillips, P.E (1975)
Environmental Contamination by lead, cadmium, zinc, and copper in a new lead producing area.
Environmental Research 9,159-172.

Dorn, C.R. Pierce, J.O. Phillips, P.E. and Chase, G.R. (1976)
Airborne Pb, Cd, Zn and Cu concentration by particle size near a lead smelter.
Atmospheric Environment 10,443-446.

Dovland, H and Eliassen, A. (1976)
Dry deposition on a snow surface.
Atmospheric Environment 10,783-785.

Duggan, M.J. and Williams, S. (1977)
Lead-in-dust in city streets.
Science of the Total Environment, 7,91-97.

Duggan, M.J. (1980)
Lead in urban dust: an assessment.
Environmental Services Division, G.L.C.
Report R84.

Duggan, M.J. and Burton, M.A.S (1983)
Atmospheric deposition in London
International Journal of Environmental Studies,21,301-307.

Dzubay, T.G. (1980)
Chemical Elemental Balance Method applied
to dichotomous sampler data
Journal of the New York Acedemy of Science 338, 126-144.

Eatough, D.J. et al (1979)
The Chemical composition of smelter flue dust
Atmospheric Environment 13,489-506.

Eckshlager, K (1969)
Errors measurement and results in chemical
analysis.
Van Nostrand, London.

Emerson, J.D. and Stoto, M.A. (1983)
Transforming data.
In 'Understanding Robust and Exploratory
Data Analysis' Ed. Hoaglin, D.C.,
Mosteller, F. and Tukey J.W.
John Wiley and Sons. USA.

Environmental Protection Agency (1977)
Compilation of Air Pollution Factors.
3rd Edition, A.P-42. Research Triangle
Park. USA.

FAO/WHO (1972)
Evaluation of certain food additives and
contaminants: Mercury, Lead and Cadmium.
16th report of the Joint FAO/WHO Expert
Committee on Food Additives.
WHO Technical Report No. 505, Gevena,

Fell, G.S. (1980)
Metals in the Environment.
Chemistry in Britain 16,323-326.

Fellowships of Engineering (1981)
Reduction of lead in the Environment,
Energy, Technology and Cost.
Report of Working Party on Lead, London.

Forland, E.J. and Gjessing, Y.T (1975)
Snow contamination from washout/rainout
and dry deposition.
Atmospheric Environment, 9,339-352.

Fox, M.R.S.(1974)
Effect of essential minerals on cadmium
toxicity: a review.
Journal of Food science 37, 321-324.

Franzin, W.G., McFarlane, G.A. and Lutz, A. (1979)
Atmospheric fallout in the vicinity of a base
metal smelter at Flin-flon,
Manitoba, Canada.
Environmental Science and Technology 13,1513-1522.

Friberg, L. Piscator, M. Nordberg G. and
Kjellstrom, T. (1974)
Cadmium in the environment.
CRC Press, Cleveland.

Friedlander, S.K. (1973)
Chemical Elemental Balances and identification
of air pollution sources.
Environmental Science and Technology, 7,235-240.

Gaarenstrome, P.D. Perone, S.P. and Moyers, J.L (1977)
Application of pattern recognition and factor
analysis for characterisation of atmospheric
particulate composition in the Southwest desert
atmosphere.
Environmental Science and Technology, 11, 795-800.

Galloway, J.N. and Likens, G.E (1976)
Calibration of collection procedures for
the determination of precipitation chemistry.
Water, Air and Soil Pollution 6,241-258.

Galloway, J.N., Eisenreich, S.J and Scott, B.C (1980)
Toxic substances in atmospheric deposition:
a review and assessment.
National Atmospheric Deposition Programme,
NC-141- USA.

Gartell, G. and Friedlander, S.K. (1975)
Relating particulate pollution to sources:
The 1972 California Aerosol Characterization Study.
Atmospheric Environment, 9,279-299.

Gatz, D.F (1975)
Relative contributions of different sources of
urban aerosols: Application of new estimation
method to multiple sources in Chicago.
Atmospheric Environment, 9,1-18.

Gatz, D.F (1978)
Identification of Aerosol Sources in the St Louis
area using Factor Analysis.
Journal of Applied Meteorology, 17,600-608.

Georgii, H.W, Perseke, G and Rohbock, E (1984)
Deposition of acid components and heavy
metals in the Federal Republic of Germany
for the period 1979-1981.
Atmospheric Environment 18, 581-589.

Gifford, F.A. and Hanna, S.R. (1971)
Urban air pollution modelling.
Second International Clean Air Congress.
pp 1146-1151.

Gifford, F.A and Hanna, S.R (1973)
Modelling Urban Air Pollution.
Atmospheric Environment 7 131-136.

Goklany, I.M. (1980)
Emission inventory errors for point sources and some quality assurance aspects.
Journal of the Air Pollution Control Association 30, 362-365.

Goodall, C. (1983)
Examining Residuals
In 'Understanding Robust and Exploratory Data Analysis'. Ed. Hoaglin, D.C, Mosteller, F and Tukey, J.W.
John Wiley and Sons, USA.

Goodman, G.T. and Roberts, I.M. (1971)
Plants and Soils as indicators of metals in the air.
Nature 231, 287-292.

Gordon, G.E. (1980)
Receptor models.
Environmental Sciences and Technology 14, 792-800.

Green, D.E. (1982)
The investigation of solid particulate aerosols in the Selby District Council Area. Phase 4, a multielement survey in the Selby district, January 1980-December 1980.
Unpublished report, CEGB.

Greenberg, R.R. Zoller, W.H. and Gordon G.E (1981)
Atmospheric emissions of elements on particles from the Parkway sewage sludge Incinerator.
Environmental Science and Technology 15,64-70.

Hallet, J. Lardinois, P. Ronneau, C and Cara, J. (1982)
Elemental deposition as a function of distance from an industrial zone.
Science of the Total Environment , 25,99-109.

Hallsworth, E.G. and Adams, W.A. (1973)
The heavy metal content of rainfall in the East Midlands
Environmental Pollution, 4,231-235.

Harman, H.H. (1967)
Modern Factor Analysis.
2nd Edition. University of Chicago Press.

Harrison, P.R. Matson, W.R. and Winchester, J.W. (1971)
Time variations of lead, copper and cadmium concentrations in aerosols in Ann Arbor, Michigan
Atmospheric Environment 5,613-619.

Harrision, R.M. (1979)
Toxic metals in street and household dusts.
Science of the Total Environment, 11,89-97.

Harrison, R.M. and Laxen, D.P.H. (1981)
Lead pollution; causes and control.
Chapman and Hall. London.

Harrison, R.M. Perry, R and Wellings, R.A. (1975)
Lead and cadmium in precipitation: their
contribution to pollution.
Journal of the Air Pollution Control Association, 25,637-630.

Heidam, N.Z. (1984)
The components of the Arctic Aerosol
Atmosperic Environment, 18,329-343.

Hendrickson, E.R. (1968)
in 'Air Pollution' 2nd ed. Vol II.
ed. Stern, A.C . Acedemic Press,
New York.

Herron, M.M. Langway, C.C., Weiss, H.V.
and Cragin, J.H. (1977)
Atmospheric trace metals and sulfate
in the Greenland Ice Sheet.
Geochim. Cosmochim. Acta. 41 915-920

Hicks, B.B et al. (1980)
Critique of methods to measure dry deposition:
workshop summary.
Argonne National Laboratory, Illinois
E.P.A. 600/9-80/050.

Hirao, Y and Patterson, C.C. (1974)
Lead aerosol pollution in the High
Sierra overrides natural mechanisms
which exclude lead from food chains.
Science 184,989-992.

Hopke, P.K. Gladney, E.J. Gordon, G.E. Zoller, W.H.
and Jones A.G. (1976)
The use of multivariate analysis to identify
sources of selected elements in the Boston Aerosol.
Atmospheric Environment, 10,1015-1025.

Hopke, P.K. Lamb, R.E. and Natusch, D.F.S. (1980)
Multielemental characterisation of urban
roadway dust.
Environmental Science and Technology 14,164-172.

Horst, T.W. (1977)
A surface depletion model for deposition from a Gaussian Plume.
Atmospheric Environment 11,41-46.

Hosker, R.P and Lindberg, S.E. (1982)
Review: Atmospheric deposition and plant assimilation of gases and particles.
Atmospheric Environment 16,889-910.

Jaworowski, Z. Bilkiewicz, J. Dobosz, E. and Wodkiewicz, L. (1975)
Stable and radioactive pollutants in a Scandinavian Glacier.
Environmental Pollution, 9,305-315.

Johnson, M. Roberts, D and Firth, N. (1978)
Lead and zinc in the terrestrial environment around derelict metalliferous mines in Wales (UK).
Science of the Total Environment, 10,61-78.

Johnston, R.J. (1978)
Multivariate Statistical Analysis in Geography.
Longman. London.

Joint Unit for Research on the Urban Environment (1980)
Walsall's Industrial Economy.
Aston University Publication.

Junge, C.E. (1963)
Air Chemistry and Radioactivity.
New York, Acedemic Press.

Kim, J.O (1975)
Factors Analysis.
Statistical Package for the Social Sciences.
Ed N.H Nie et al
McGraw and Hill, New York.

Lagerwerff, J.V and Specht, A.W. (1970)
Contamination of roadside soil with cadmium, nickel, lead and zinc.
Environmental Science and Technology 4,583-586.

Lansdowne, R., Yule, W. Urbanowicz, M.A. and Millar, I.B (1983)
Blood-lead, intelligence, attainment and behaviour in school children: overview of a pilot study.
In 'Lead V.S. Health: sources and effects of low-level lead exposure.
Ed. Rutter, M. and Russell-Jones, R.
John Wiley and Sons, Chichester.

Lauwreys, R. Roels, H. Bernard, A. and Buchet, J.P (1980)
Renal response to cadmium in a population living in a non-ferrous smelter area in Belgium.
International Archives of Occupational and Environment Health, 45, 271

Lauwerys, R.R. (1981)
Health Effects of Cadmium.
In 'Trace metals: Exposure and health Effects' Ed. E.de Ferrante.
CEC Luxembourg.

Lazarus, A.L. Lorange, E. and Lodge, J.P (1970)
Lead and other metal ions in United States Precipitation.
Environmental Science and Technology, 4,55-58.

Lee, R.E. Patterson, R.K. and Wagman, J. (1968)
Particle size distribution of metal components in urban air.
Environmental Science and Technology 2,288-290.

Lewis, G.P (1972)
Cigarette Smoking and Cadmium Accumulation in Man.
Lancet i (March 25),682-683.

Lindberg, S.E. Andren, A.W. Raridon, R.J and Fulkerson W. (1975)
Mass Balance of trace Elements in Walker Branch watershed: Relation to coal-fired power.
Environmental Health Perpectives 12,9-18.

Lindberg, S.E. Turner, R.R, Shiner, D.S. and Huff, D.D (1981)
Atmospheric deposition of heavy metals and their interaction with acid precipitation in a North American deciduous forest.
In 'Heavy metals in the Environment'.
Proceedings of the 3rd International Conference on Heavy Metals. Amsterdam, CEC/WHO.

Linton, R.W. Natusch D.F.S. Hopke, P.K and Solomon, R.L (1977)
The use of microscopic and bulk analysis as a multi-technique approach to determine the sources of urban dust.
4th Joint Conference on Sensing of Environmental Pollutions, New Orleans .

Liteanu, C. and Rica, I. (1980)
Statistical Theory and Methodology
of Trace Analysis.
John Wiley and Sons. Chichester.

Little, P (1973)
A study of Heavy Metal contamination of
leaf surfaces.
Environmental Pollution 5,159-172.

Little, P and Martin, M.H (1972)
A survey of zinc, lead and cadmium in soil
and natural vegetation around a smelting
complex.
Environmental Pollution 3,241-254.

——————— (1974)
Biological monitoring of heavy
metal pollution.
Environmental Pollution 6,1-19.

Little, P. and Wiffen, R.D. (1977)
Emission and deposition of petrol
engine exhaust Pb: 1, Deposition
of exhaust Pb to plant and
soil surfaces.
Atmospheric Environment 11,437-447.

——————— (1978)
Emission and deposition of petrol
engine exhaust Pb: 2, Airborne
concentration of lead near motorways.
Atmospheric Environment 12,1331-1341.

Lucas, D.H (1957)
Certain aspects of the deposition of dust.
Journal of the Institute of Fuel, Nov,623-627.

Mantle, E.C. (1973)
The secondary metals industry and the environment.
Clean Air. Summer,

Mantle, E.C (1974)
Prevention of air pollution in the
non-ferrous metals industries.
BNF Technology Centre, London

McCrone, W.C. (1976)
The particle atlas.
Ann Arbor Sciences Inc.

McDonald, C. and Duncan, H.J (1979)
Particle size distribution of metals
in the atmosphere of Glasgow.
Atmospheric Environment 13,977-980.

McInnes, G. (1979)
Multi elemental survey: 1,analysis of
the first two years results.
Warren Spring Laboratory. Stevenage LR305 (AP).

McMahon, T.A. and Denison, P.J. (1979)
Empirical atmospheric deposition parameters:
a survey.
Atmospheric Environment 13,571-585.

Merry, R.H. Tiller, K.G. De Vries, M.P.C.and
Cartwright, B. (1981)
Contamination of wheat crops around a lead
zinc smelter.
Environmental Pollution B2 37-48.

Millar, C.R., Schroeder, S.R. Mushak, P. and
Boone, L. (1981)
Failure to find hyperactivity in
preschool children with moderately
elevated lead burden.
Journal of Pediatric Psychology 6,85-95.

Millar, M.S. Friedlander, S.K. and Hidy, G.M (1972)
A Chemical Elemental Balance for the
Pasadena aerosol.
Journal of the Air Pollution Control Association
39 165-176.

Minczewski, J. Chwastowska, J. and Dybczynski, R (1982)
Separation and preconcentration methods in inorganic
trace analysis.
Ellis and Horwood Ltd Chichester.

Ministry of Agriculture Fisheries and Food (1981)
Survey of lead in food: second supplementary
report.
Food surveillance report No. 10, HMSO.

Muller, J. and Beilke, S. (1977)
Wet removal of heavy metals from the atmosphere.
In 'Proceedings of the International Conference
on Heavy metals in the Environment'
Toronto, Ontario pp 987-999.

Muskett, C.J. (1976)
A survey of airborne heavy metals in a city environment using biological indicators. Environmental Health, 84, 267-269.

Muskett, C.J. and Jones, M.P. (1980)
The dispersal of lead, cadmium and nickel from motor vehicles and effects on roadside invertebrate macrofauna.
Environmental Pollution A23,231-242.

Needleman, H.L (1979)
Deficits in psycological and classroom performance of children with elevated blood lead levels.
New England Journal of Medicine. 300,689-695.

Nieboer, E. and Richardson, D.H.S (1980)
The replacement of the non-descript term 'heavy metals' by a biologically and chemically significant classification of metal ions.
Environmental Pollution B1,3-26.

Nogawa, K. (1981)
Itai-itai disease and follow-up studies.
In 'Cadmium in the Environment: Part 2"
Ed. J.O. Nriagu, John Wiley and Sons.

Nriagu, J.O. (1978)
The biogeochemistry of lead in the environment'.
Elsevier/North-Holland Biomedical Press, Amsterdam.

Nriagu, J.O. (1979)
Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere.
Nature 279,409-411.

Orlemann, J.A. et al (1983)
Fugitive dust control technology.
Noyes Data Corporation, New Jersey.

Pacyna, J.M. (1984)
Estimation of the atmospheric emissions of trace elements from anthropogenic sources in Europe.
Atmospheric Environment 18,41-45.

Passow, H. Rothstein, A. and Clarkson, T.W. (1961)
The general pharmacology of heavy metals.
Pharmacology Review 13, 185-224.

Pattenden, N.J (1974)
Atmospheric concentrations and deposition
rates of some trace elements measured in
the Swansea/Neath/Port Talbot area.
A.E.R.E. Harwell R-7729.

Pattenden, N.J. and Branson, J.R. (1982)
Multielement airborne dust and deposition
measurements at 76 Primley Avenue, Walsall;
Report for the year August 1980-July 1981.
A.E.R.E. Harwell HL/82/1702

Peirson, D.H. Cawse, P.A. Salmon, L
and Cambray, R.S. (1973)
Trace elements in the atmospheric environment.
Nature 241,252-256.

Perry, R. and Young R. (1977)
Handbook of Air Pollution Analysis.
Chapman and Hall, London.

Pinta, M. (1973)
Detection and determination of trace elements.
5th Edition. Ann Arbor Science. London

Pocock, R.L. (1982)
Background levels of heavy metal soil
contamination in Walsall.
University of Aston, Birmingham

Pocock, R.L. and Simmons, S.A. (1984)
Airborne deposition of metals to land
Paper presented to International Environment
and Safety Conference, London.

Ragland, K.W. (1973)
Multiple Box model for dispersion
of pollutants from area sources.
Atmospheric Environment 7,1017-1032.

Ralph, M.O. and Barrett, C.F. (1976)
A Wind-tunnel study of the efficiency
of deposit gauges.
Warren Spring Laboratory, LR 235 (AP).

Remington, R.D. and Schork, M.A. (1970)
Statistics with applications to the
Biological and Health Sciences.
Prentice Hall, New Jersey.

Roberts, T.M et al (1976)
Lead accumulation around secondary
lead smelters: Estimation of dispersal
and accumulation by humans.
Science 186, 1120-1123.

Rohbock, E. Georgii, H.W. Perseke, C and
Kins, L (1981)
Wet and dry deposition of heavy metals
aerosols in the Federal Republic of Germany.
In 'Heavy metals in the Environment'
Proceedings of the 3rd International
Conference on heavy metals. Amsterdam.

Royal Commission on Environmental Pollution (1983)
Lead in the Environment
9th Report, HMSO. London.

Rummel, R.J. (1970)
Applied Factor Analysis.
North Western University Press.

Rupp, E.M. et al (1978)
Composite hazard index for assessing
limiting exposures to enviromental
pollutants: Application through a
Case-study.
Environmental Science and Technology 12, 802-807.

Salmon, L. et al (1978)
Retrospective trend analysis of the content
of U.K air particulate matter,
1957-1974.
Science of the Total Environment 9, 161-200.

Schlesinger, W.H. Reiners, W.A. and Knopman D.S (1974)
Heavy metal concentrations and deposition
in bulk precipitation in montane ecosystems
of New Hampshire USA.
Environmental Pollution 6, 39-47.

Sharma, V. (1976)
An area-source model for urban air pollution
applications.
Atmospheric Environment, 10, 1027-1032.

Shaw, F.M (1972)
Iron foundry air pollution in the United Kingdom.
The British Foundryman, 65,90-105.

Slanina, J. Van Raaphorst, J.G. Zijp, W.L
Vermeulan, A.J and Roet, C.A. (1979)
An evaluation of the chemical composition
of precipitation sampled with 21 identical
collectors in a limited area.
International Journal of Environmental Analytical
Chemistry 6,67-81.

Snyder, M.K and Shobe, F.O (1980)
Source category survey; Secondary
Copper Smelting and Refining.
EPA 450/3-80/0011 Research Triangle Park.

Som,R.K. (1973)
A manual of sampling techniques.
Heinemann, London.

Struempler, A.W. (1976)
Trace metals in rain and snow during
1973 at Chadron, Nebraska.
Atmospheric Environment, 10,33-37.

Ter Haar, G.L. Holtzman, R.B. and Lucas, H.F. (1967)
Lead and lead-210 in rainwater.
Nature 216,353-355.

Tennant, C.J (1984)
Cadmium in the Environment and High
Risk Population Groups.
Thesis. University of Aston Birmingham.

Thatcher, R.W. Lester, M.L. McAlaster, R. and
Holst, R (1982)
Effects of low levels of cadmium and
lead on the cognitive functioning in
children.
Archives of Environmental Health 37,159-166.

Tunnicliffle, M.F. (1973)
Scrap and The Environment.
Clean Air,Summer,18-29.

Tucker A. (1972)
The Toxic Metals.
Earth Island,London.

Turner, A.C. Carroll, J.D. and Barrett, C.F (1980)
The determination of environmental lead near works and roads in conjunction with the EEC blood-lead survey 1978-1979.
Warren Spring Laboratory,LR 344 AP.

Turner, D.B (1979)
Atmospheric dispersion modelling:
a critical review.
Journal of the Air Pollution Control Association
5,502-519.

Turner, D.B, Zimmerman, J.R and Busse, A.D (1972)
An evaluation of some climatological dispersion models.
In 'Proceedings of the 3rd meetings of the Expert Panel on Air Pollution Modelling. NATO/CCMS.

Tyler, G (1978)
Leaching rates of heavy metal ions in forest soils.
Water, Air and Soil Pollution, 9,137-148.

Underwood, E.J (1977)
Trace elements in Human and Animal Nutrition.
4th Edition. Academic Press. London.

Vanderborght, B, Mertens,I. and Kretzschmar, J (1983)
Comparing the calculated measured aerosol concentrations and depositions around a metallurgical plant.
Atmospheric Environment, 17,1687-1701.

Vandergrift, A.E et al (1971)
Particulate Air Pollution in the United States.
Journal of the Air Pollution Control Association
21,321-328.

Vincent, J.H. Hutson, D., and Mark, D. (1982)
The nature of air flow near the inlets of blunt dust sampling probes.
Atmospheric Environment 16,1243-1249.

Walsall Environmental Health Department (1983)
Reports of analyses of road and playground dusts. Personnal Communications.

Wallin, T. (1976)
Deposition of airborne mercury from six Swedish Chlor-alkali plants surveyed by moss analysis.
Environmental Pollution 10,101-114.

Ward, J.H (1963)
Heirarchical grouping to optimize an objective function.
Journal of Americal Statistical Association 58,491-501.

Warda, R.D. and Buhr, R.K (1973)
A method of sampling cupola emissions.
Transactions of the American Foundry Society 81,24-37.

Waughman, G.J. and Brett, T. (1980)
Interference due to major elements during estimation of trace heavy metals in natural materials by atomic absorption spectrophotometry.
Environmental Research 21,385-393.

Weber, E. (1981)
Air Pollution Control Strategy in the Federal Republic of Germany.
Journal of the Air Pollution Control Association 31,24-30.

Whitby K.T (1978)
The physical characterisation of sulphur aerosols.
Atmospheric Environment. 12,135-159.

Willeke, K. and Whitby, K.T. (1975)
Atmospheric aerosols: size distribution interpretation.
Journal of the Air Pollution Control Association 25,529-534.

Wishart, D. (1982)
Clustan User Manual: Version 2
Release 1.
University of Edinburgh.

World Health Organisation (1977)
Environmental Helth Criteria for Cadmium.
Ambio.

World Health Organisation (1982)
Rapid assessment of sources of air water and land pollution.
WHO Offset Publication No. 62, Geneva.

Yeomans, K.A. (1968)
Statistics for the Social Scientist: 1
Penguin Education.

Younden, W.J. (1952)
Statistical methods for chemists.
John Wiley and Sons, Canada.